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# Gas sorption by soils and clay minerals

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GAS SORPTION BY SOILS AND CLAY MINERALS

by

Francis Shigeru Nakayama

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Soil Fertility

Approved:

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## INTRODUCTION

The aeration status of soils has often been characterized by the composition of the soil air and the rate of diffusion of gases through the soils. Black (10, p. 94) has pointed out, however, that the solubility and diffusion rates of gases in the water films surrounding root surfaces need to be considered also. The diffusion coefficient of  $O_2$  is  $0.17 \text{ cm.}^2/\text{sec.}$  in air, whereas it is only  $1.75 \times 10^{-5} \text{ cm.}^2/\text{sec.}$  in water (85, vol. 5, p. 62). At  $25^\circ\text{C.}$  and 760 mm. of Hg pressure, 1000 cc. of pure water dissolve 17.08 cc. of air of which 5.78 cc. is  $O_2$  (43, p. 1479). Thus, it can be seen that the volume of dissolved air and the rate of gas movement in the water in soils are quite small compared with the gas phase.

If electrolytes or non-electrolytes are added to water, the solubility of air may be decreased. Therefore, it is expected that soil water, which is in the environment of soil colloidal particles, exchangeable cations and other dissolved materials, may not dissolve as much air as pure water. Furthermore, the water in unsaturated soils is subjected to capillary forces which may also modify the solubility of air.

The colloidal material in soils is capable of adsorbing the gases in air when the soils are quite dry. Thus, the amount of gas taken up by partially dried soils will be de-

terminated by the amount adsorbed as well as the amount dissolved in the soil water. The term sorption will be used to include both adsorption and absorption (solution).

The objective of this investigation was to determine the sorption of gases by soil and clay mineral systems at different moisture levels and to relate the amount sorbed to the solubility of the gases in the water present. Attention was also given to the gas adsorption characteristics of dry soils and clay minerals and the effect of water on the amount of gas sorbed by these materials at low moisture levels. This investigation was confined to the use of  $O_2$  and  $CO_2$ .

## REVIEW OF LITERATURE

## Solubility of Gases in Water

The solubility of a gas in water can be expressed by Henry's equation  $P_G = kX_G$ , where  $P_G$  is the partial pressure of the gas,  $k$  is Henry's constant and  $X_G$  is the mole fraction of the gas in solution (42, p. 26). There has been a notable lack of agreement concerning the solubility data of gases in liquids. Markham and Kobe's (58) review on this subject, which includes over 350 citations, adequately covers the problems encountered with the different methods of determining gas solubility and points out the more reliable results. The following values for Henry's constant which were calculated from those given in the Handbook of Chemistry and Physics (43, p. 1480) were used in this investigation. They compare favorably with those reported elsewhere (85, vol. 3, p. 257).

Table 1. Henry's law constant for the solubility of different gases in water at 25° C.<sup>a</sup>

| Gas             | Henry's constant (mm.)  |
|-----------------|-------------------------|
| O <sub>2</sub>  | 3.24 X 10 <sup>7</sup>  |
| CO <sub>2</sub> | 0.124 X 10 <sup>7</sup> |
| He              | 11.0 X 10 <sup>7</sup>  |

<sup>a</sup>Interpolated from values given for 20° and 30° C. (43, p. 1480)

It has been observed that the solubility of gases in water may be decreased by the addition of electrolytes and non-electrolytes and that the relative decrease is the same for different gases. This decrease in gas solubility from added solutes is commonly referred to as the "salting-out" effect. Fox (31) and Whipple and Whipple (86) measured the solubility of  $O_2$  in sea water and found it was related to the chloride concentration. Akerl f (2) and MacArthur (54) noted that the addition of several different electrolytes decreased the solubility of He and  $O_2$ . Parts of MacArthur's (54) data are listed below in Table 2 to show the effect of different salts and their concentration on  $O_2$  solubility.

Table 2. Effect of different salts and their concentration on the solubility of  $O_2$  in water equilibrated with air at 25  C. and a pressure of 760 mm. of Hg.  
Data from MacArthur (54)

| Salt and concentration | Solubility of $O_2$ ,<br>cc./l |
|------------------------|--------------------------------|
| $H_2O$                 | 5.78                           |
| m/8 LiCl               | 5.63                           |
| m/4 "                  | 5.49                           |
| m/2 "                  | 5.17                           |
| m "                    | 4.59                           |
| 2m "                   | 3.63                           |
| m/8 NaCl               | 5.52                           |
| m/4 "                  | 5.30                           |
| m/2 "                  | 4.92                           |
| m "                    | 4.20                           |
| 2m "                   | 3.05                           |
| m/8 KCl                | 5.52                           |
| m/4 "                  | 5.30                           |
| m/2 "                  | 4.98                           |
| m "                    | 4.26                           |
| 2m "                   | 3.21                           |

Randall and Failey (69) have also tabulated the effect of a great number of electrolytes on the solubility of  $O_2$ ,  $H_2$ ,  $N_2$ ,  $N_2O$ ,  $CO_2$ ,  $NH_3$  and  $C_2H_2$ .

Müller (64) and Usher (81) found that non-electrolytes also decrease the solubility of gases in water. The effect of sucrose on the solubility of  $CO_2$  observed and expressed in terms of the Bunsen coefficient by Usher (81) is shown in Table 3. The Bunsen coefficient is the volume of gas reduced to  $0^\circ C.$  and 760 mm. of pressure of Hg which is absorbed by the unit volume of liquid when the partial pressure of the gas is 760 mm.

Table 3. Effect of sucrose on the Bunsen coefficient of  $CO_2$  in water. Data from Usher (81)

| Sucrose<br>concentration | Bunsen<br>coefficient |
|--------------------------|-----------------------|
| --                       | 0.877                 |
| N/8                      | 0.846                 |
| N/4                      | 0.815                 |
| N/2                      | 0.756                 |
| N                        | 0.649                 |

According to Daniels and Alberty (18, p. 201), a good theoretical explanation for the solubility of inert gases in liquids has not been fully developed. They state, however, that the solubility of gases is probably due to an attractive



force between the gas and solvent molecules due to dipole-induced dipoles. When another solute is added to the water, the polar water molecules can be considered to be oriented with respect to the ions or dipoles of the dissolved material and thus to be less free to induce dipoles in the gas molecules. More simply, the "salting-out" effect may be explained on the hypothesis that it is caused by the hydration of the solute and this water can no longer act as a solvent to absorb the gas.

Albright and Williams (3) have treated the "salting-out" effect due to electrolytes in terms of the attraction of the medium of highest dielectric, which is usually water, by the solute ion. Since the water is attracted preferentially into the field about the ion, the less polar material will be forced further from the ionic field. Furthermore, since the outer field can dissolve only a certain amount of the gas, the net result is that a smaller amount of gas will be dissolved by the water as a whole.

The "salting-out" effect from colloidal materials has not been as extensively studied as that for soluble materials. King (48) felt that colloidal solutions in general should decrease the gas solubility provided that adsorption or chemical combination of the gas with the colloidal materials did not occur.

Findlay and co-workers (26, 27, 28, 29, 30) made a systematic study on the effect of colloids and suspensions upon the solubility of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{O}_2$  and  $\text{N}_2$ . Their results were inconsistent in that with some colloidal solutions the gas solubility was less while in others it was greater than that in pure water. The solubility of gases in the colloidal solutions did not follow Henry's law. In general, where the solubility was increased, the solubility curve fell with increasing pressure; and, where the solubility was decreased, the solubility curve rose with pressure. In comparison, the solubility of gases in salt solutions was less than that in pure water, but it followed Henry's law.

The solubility of gases in soil water would be expected to be modified from that in pure water due to the hydration of clay minerals, exchangeable cations and other dissolved materials. References have been made to the solubility of gases in soil water in several adsorption studies with soils. Lubatti and Smith (52) found a steady rise in sorption of methyl bromide as the soil approached water saturation. Hanson and Nex (37) reported an increase in ethylene dibromide sorption by moist soil when the moisture level was increased and presumed that it was due to the solution of ethylene dibromide in the soil water. A direct comparison of the sorption values and the values for the gas solubility in the soil water was not made in these investigations.

Call (16) and Wade (82) found that the quantities of ethylene dibromide sorbed by soils at moisture contents above 20% were approximately three times greater than that which could be accounted for by the solution of the gas in the soil water. Call (15) has suggested that part of the ethylene dibromide could be sorbed on the water interface, while Wade (82) believed that the gas was dissolved in solution and adsorbed on the soil particles at the same time.

Runkles et al. (73) observed that the amount of  $O_2$  sorbed by moist vermiculite containing 50 to 300% moisture was equivalent to the  $O_2$  that would theoretically dissolve in the soil water if the water behaved as pure water. The amount of  $O_2$  sorbed by a moist Edina subsoil sample that contained 10 to 25% moisture was, however, less than the solubility values.

### Adsorption

The general theories of adsorption have been discussed in detail in the textbooks of Adam (1), Brunauer (14) and McBain (55). The more recent developments in this field have been reviewed by Harris (38, 39, 40, 41) and Ries (70).

Kuron (49) was one of the earliest workers to study the adsorption of gases and vapors by soils. He found that clays which were vacuum-dried at  $100^\circ C.$  over  $P_2O_5$  adsorbed less  $CO_2$  than those dried at room temperature over concentrated

H<sub>2</sub>SO<sub>4</sub>. The adsorptive capacity of soils receiving the same treatment was, however, the same. Other investigators have reported that the adsorptive capacities of soils and silicate minerals usually increase when the samples are dehydrated.

Wiesmann and Neumann (88) observed an increase in the adsorption of N<sub>2</sub>, O<sub>2</sub> and air by soils when the soil moisture was decreased from 7 to 4%. Jamison (44) obtained a larger adsorption of air by oven-dried soils than moist soils. The adsorptive capacity of chabasite for O<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub> was found by Lamb and Woodhouse (50) to increase gradually to a maximum when increasing increments of water were removed from the sample and to decrease when all of the water was removed. Evans (24) also found that the dehydrated chabasite adsorbed a greater quantity of NH<sub>3</sub> than the hydrated chabasite.

Chisholm and Koblitsky (17), and Lubatti and Smith (52) demonstrated that dry soils adsorb more methyl bromide than wet soils. Stark (76) studied the adsorptive capacities of soils that had been exposed to different relative humidities and found greater adsorption of chloropicrin by the samples that had less moisture.

Hanson and Nex (37) observed that a minimum adsorption of ethylene dibromide in soils occurred slightly below the wilting point of the soils with a marked increase at the lower moisture levels and a slow increase at the higher mois-

ture levels. Wade (83) and Call (15, 16) also using ethylene dibromide found the initial small increase in moisture content of soils from their oven-dried state caused a sharp decrease in adsorption. The rate of decrease was smaller as the moisture content was increased, passed through a minimum and then increased slightly with increasing moisture content. Stanley and Smith (75) reported that the retention of anhydrous ammonia was greatest between 15 to 18% moisture with increased loss at higher and lower moisture contents.

Other independent investigations have pointed out the importance of the structure of the adsorbent, and the role of the water in relation to the accessibility of the adsorbing surfaces. Elkin (19) found that the size of the clay aggregate did not materially influence the amount of benzene vapor adsorbed and he suggested that the aggregate contained pores that were large enough to permit the benzene molecule to reach the surface of the primary particles. Barrer (7) noted that open-structured, three dimensional zeolites adsorbed a large amount of non-polar gases ( $H_2$ ,  $O_2$ ,  $N_2$ ), whereas the fibrous and platy zeolites did not. The larger gas molecules could not penetrate the lattice of the latter types of zeolites.

Escard (22) studied the influence of residual water on the accessible surfaces of montmorillonite. Maximum surface

areas were observed at moisture contents of 6 to 10% in Na and Ca montmorillonites. In a similar type of investigation, Brooks (13) observed from  $N_2$  adsorption measurements that the surface area of montmorillonite and illite depended on the water content, whereas kaolinite and pyrophyllite did not. Nitrogen adsorbed by the bentonite decreased when it was degassed at temperatures above  $600^{\circ} \text{C}$ .

Lopez-Gonsalez and Dietz (51) noted a fairly constant amount of  $N_2$  adsorption when bentonite was dried between  $200^{\circ}$  to  $600^{\circ} \text{C}$ . and a rapid drop when it was dehydrated above  $700^{\circ} \text{C}$ . The bentonite adsorbed a negligible amount of  $N_2$  after it was heated at  $900^{\circ} \text{C}$ . Wieden and Balduin (87) found a gradual drop in  $\text{CO}_2$  adsorption for bentonite heated from  $100^{\circ}$  to  $600^{\circ} \text{C}$ . The  $N_2$  adsorption of Na-rich montmorillonite was found by Barrer and McLeod (8) to increase slightly when samples were heated to  $250^{\circ} \text{C}$ ., but  $\text{NH}_3$  adsorption decreased. The authors attributed this to a decrease in the ability of  $\text{NH}_3$  molecules to penetrate between the layers of the clay mineral.

The kaolinite surface area measured by Brooks (13) using  $N_2$  remained essentially constant up to a degassing temperature of  $800^{\circ} \text{C}$ . Gregg and Stephens (35) also found very little change in the surface area of kaolinite over a range of  $50^{\circ}$  to  $800^{\circ} \text{C}$ . even though the mineral lost some of its

structural water.

Nelson and Hendricks (65) found little change in the adsorptive capacity of kaolinite and illite when they were degassed up to  $700^{\circ}$  C., but a decrease occurred when they were heated to  $900^{\circ}$  C. These workers believed that the loss of water occurred without an essential change in the crystal surface even though X-ray diffraction patterns indicated a change in crystallinity.

With materials like halloysite and Ca bentonite where there is some internal structure, Brooks (13) found evidence of hysteresis in the adsorption-desorption  $N_2$  isotherms at  $-195^{\circ}$  C. which varied with the state of hydration of the materials. Barrer and McLeod (8) also noted hysteresis in Na montmorillonite. The non-polar gases ( $N_2$  and  $O_2$ ) exhibited hysteresis loops which closed at intermediate relative pressures while the polar gases ( $NH_3$ ,  $H_2O$ ,  $CH_3OH$ ) exhibited hysteresis down to very low relative pressures. This behavior was in part associated with interlamellar adsorption.

The nature of the adsorbed water on clay surfaces is still not well understood. Grim (36, p. 162) has reviewed some of the earlier work in this field. According to Escard (23) and Mering (60) the water in monovalent cation saturated expanding type clays is fixed on the O atoms which form the

exterior layer of each plate. The water of hydration thus forms a monomolecular layer over the entire surface of the clay. Additional water forms 2, 3 and 4 layers between the plates. With the polyvalent cation saturated clays, however, the water first forms a hexahydrate octahedron around the cation and covers only part of the surface layer and also separates the plates. Additional water molecules are then arranged into two layers which further separate the plates and finally the vacant spaces are filled similar to the monovalent cation clays. This concept for polyvalent cation saturated clays conforms with Marshall's (59) general concept that the water molecules first congregate around the charged cations or O atoms which hold the layers together instead of being evenly distributed over the surface. The vacant spaces created may then be filled by additional water or other adsorbable molecules.

There is evidence to show that the clay size fraction in soils is the major adsorbing constituent. Robinson (71) found a fairly good correlation between the water adsorptive capacity of soils and their clay content. Makower et al. (57), Nelson and Hendricks (65), Stark (76) and Mortland (63) also observed a good relationship between the clay content and adsorptive capacity for a variety of gases like  $N_2$ ,  $O_2$ ,  $NH_3$  and chloropicrin.



Variable reports have been made regarding the adsorptive capacity of the organic matter in soils. Bower and Gschwend (11) indicated that the total surface area of soils measured with ethylene glycol was increased by an average value of  $7 \text{ m}^2/\text{g.}$  by each percent of organic matter present. Jamison (44) reported low adsorption of air and  $\text{O}_2$  by the oven-dried organic colloids separated from a sandy soil. Chisholm and Koblitsky (17) observed that dried peat soils adsorbed approximately twice the amount of methyl bromide than did clay soils.

Stark (76) found that relatively small amounts of chloropicrin were physically adsorbed by dry muck and peat. Siegel et al. (74) reported high adsorption of 1,3-dichloropropane and 1,2-dibromoethane by air-dried muck in comparison to bentonite or soil and that only a small proportion of the vapor could be desorbed.

Jurinak and Volman (46) observed low ethylene dibromide adsorption by a  $105^\circ \text{C.}$  oven-dried peaty muck. They ascribed this low adsorption to the inaccessibility of the internal surfaces to the vapor. Call (16) and Wade (82), on the other hand, stated that the adsorption of ethylene dibromide by soils at their field capacity could be correlated with the organic matter content. Mortland (62) also found that oven-dried muck adsorbed large quantities of  $\text{NH}_3$  due to its pene-

tration into the internal surfaces.

The results indicate that the polar molecules are adsorbed to a greater extent than the non-polar ones by the organic materials in the soils.

## MATERIALS AND METHODS

## Apparatus

The amount of gas sorbed by soils and clay minerals was determined using a volumetric method. A diagram of the apparatus and a photograph of the actual equipment in the laboratory are shown in Figures 1 and 2, respectively. The descriptive material of Barr and Anhorn (6), Joy (45) and Kuron (49) provided aid in the design and use of the apparatus.

The essential parts of the apparatus are (1) the manifold T to which the different sections were connected by means of the ground-glass ball joints  $J_1$  to  $J_5$ , (2) the sample flask F, (3) the two series of calibrated volumetric bulbs  $V_1$  to  $V_6$ , and  $V_7$  to  $V_{11}$ , (4) the burette B, (5) the manometer M, (6) the leveling bulbs  $L_1$  to  $L_4$ , (7) the high vacuum stopcocks  $S_1$  to  $S_7$  and (8) the plexiglass water jackets W.

The manifold T was constructed from heavy-walled 2 mm. diameter pyrex capillary tubing.

Pyrex glass tubing 4 to 5 cm. in diameter and 20 to 40 cm. long was used to construct sample flasks F of different sizes. The sample flask was connected to the manifold T with a No. 28 ground-glass ball joint.

Figure 1. Diagram of scruption apparatus

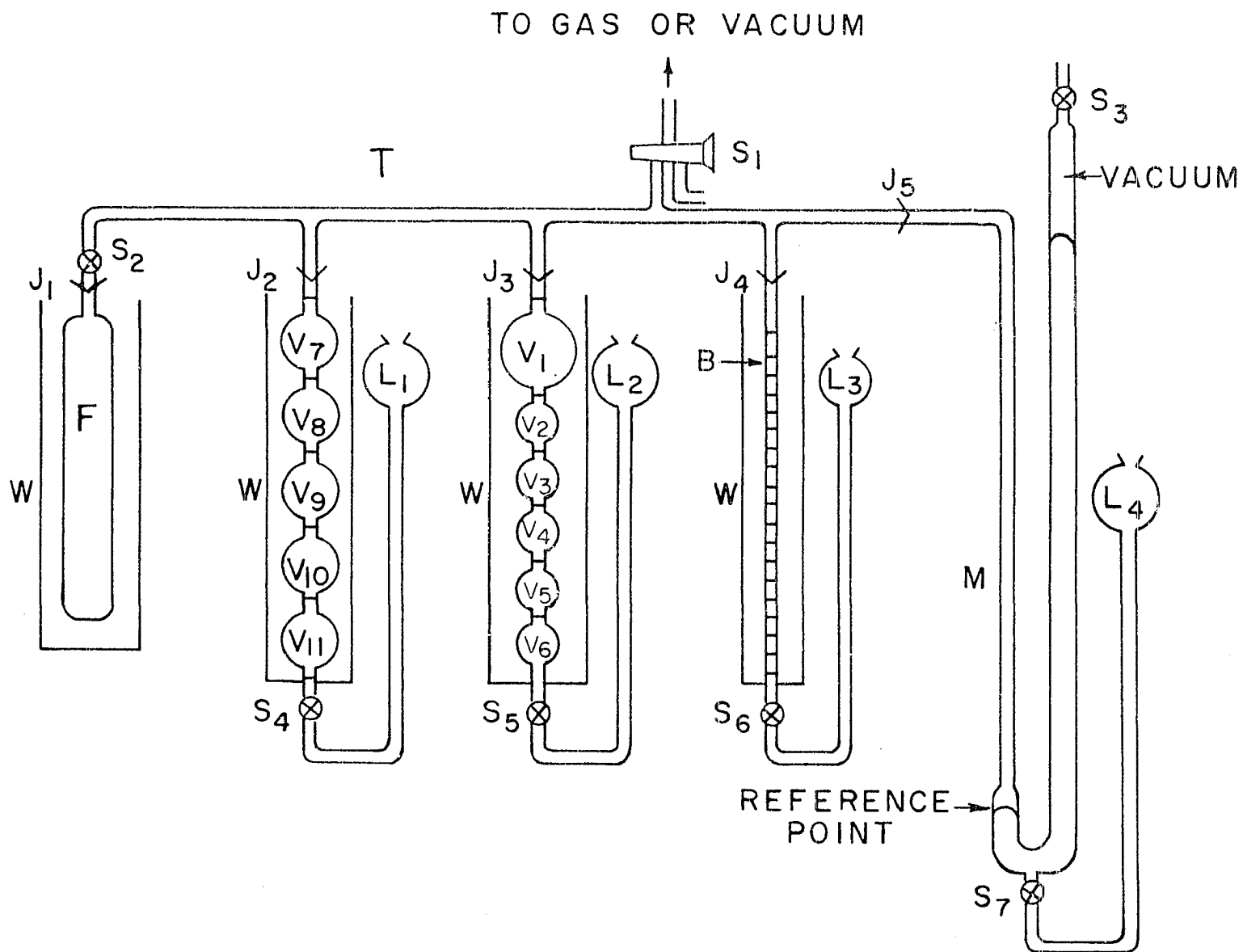
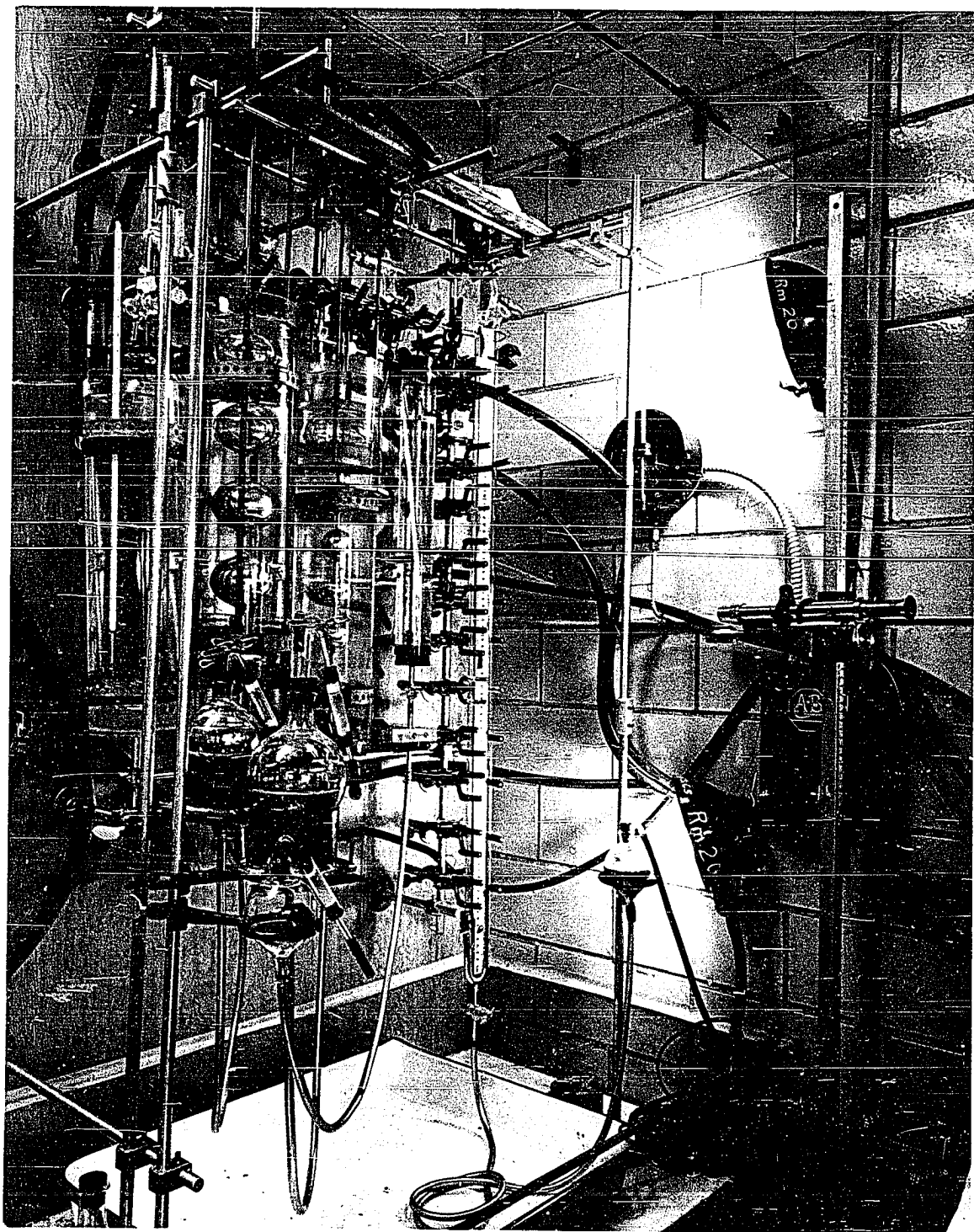


Figure 2. Photograph of sorption apparatus in the laboratory



Bulb  $V_1$  had a capacity of approximately 200 cc., bulbs  $V_2$  to  $V_6$  about 20 cc. and bulbs  $V_7$  to  $V_{11}$  about 100 cc. These volumetric bulbs were calibrated with Hg. Volumetric bulbs  $V_1$  and  $V_{11}$  were seated on separate plexiglass plates that were form-fitted to the bulbs and the plates were then connected to over-head hangers. Without this support the large weight of Hg that was drawn into the volumetric bulbs broke the waxed seals at  $J_2$  and  $J_3$ . A 10 cc. volumetric burette B with 0.05 cc. graduations was used in conjunction with the larger volumetric bulbs.

The volumetric bulbs were connected to the manifold T with No. 12 ground-glass ball joints ( $J_2$ ,  $J_3$ ,  $J_4$ ). It was convenient to employ these joints even though the number of possible leakage spots was increased because any section of the apparatus could be detached for cleaning or repair without dismantling the apparatus completely. Apiezon-W wax was used on the ball joints except  $J_1$  where Dow-Corning high vacuum was substituted.

The manometer M was constructed from 2 mm. capillary and 10 mm. diameter pyrex glass tubings. It was connected to the manifold through joint  $J_5$ . The manometer was long enough to measure pressures up to 825 mm. of Hg. It was evacuated through stopcock  $S_3$  and a vacuum was maintained in the right arm (see Figure 1) so the pressure in the apparatus



could be measured independently from the atmospheric pressure. The Hg in the manometer was adjusted to a convenient reference point within the 10 mm. tubing for the pressure measurements. A cathetometer with a precision of  $\pm 0.1$  mm. and a range of 1000 mm. was utilized.

The sorption measurements were made at  $25^{\circ}$  C. To do this, the apparatus was set up in a constant temperature room which was maintained at  $25^{\circ} \pm 1^{\circ}$  C. For even better temperature control, the sample flask and volumetric flasks were surrounded with plexiglass jackets and water from a constant temperature water bath was circulated through the system by means of centrifugal pump. The temperature of the water was maintained at  $25^{\circ} \pm 0.1^{\circ}$  C.

Stopcock  $S_1$  was a 2 mm., 2-way high-vacuum stopcock; stopcocks  $S_2$  and  $S_3$  were 2-mm. high-vacuum stopcocks with vacuum cups; and stopcocks  $S_4$  to  $S_7$  were 2-mm., straight-bore high-vacuum stopcocks. Apiezon-N grease was used on the stopcocks.

A Welch duo-seal vacuum pump was employed for the evacuation of the system. An alcohol, dry-ice vapor trap for  $H_2O$  and Hg was installed between the pump and the apparatus.

#### Gas Sorption Measurements

The soil and clay mineral samples were placed in the sample flask F and the amount of  $O_2$  or  $CO_2$  sorbed was deter-

mined either by a constant pressure or a constant volume method. The constant pressure method was used to measure the amount of gas sorbed at a single pressure. The constant volume method was used when the amount of gas sorbed at several different pressures was determined for sorption isotherms. When moist samples were used, water vapor contributed to the total gas pressure in the apparatus when equilibrium was established. Therefore, to determine the amount of gas sorbed at a specified partial pressure of that gas, the vapor pressure of the water in the moist sample had to be determined first.

#### Water vapor pressure measurements

The volumetric bulbs  $V_1$  to  $V_{11}$  and the burette B were filled with Hg. With stopcock  $S_2$  in a closed position the apparatus was evacuated through stopcock  $S_1$ . Stopcock  $S_2$  was then opened intermittently for short periods during the evacuation to remove sorbed gases from the moist soil or clay mineral sample. Stopcocks  $S_1$  and  $S_2$  were closed after the apparatus was evacuated and the temperature of the system allowed to equilibrate. Stopcock  $S_2$  was then opened and the vapor pressure of the sample was determined by measuring the change in pressure in the apparatus with the manometer.

The intermittent evacuation procedure was used to keep the loss of water from the moist samples to a minimum. As

a result it was possible to determine the water vapor pressure and then the sorption of gases by moist samples at approximately the same moisture content.

#### Constant pressure method

When dry samples were used Hg was drained from the volumetric bulbs and the burette until the volume of the empty bulbs approximated the dead space (volume not occupied by the sample in sample flask) and the system was evacuated with stopcock  $S_2$  open. When moist samples were used, the volumetric bulbs were filled with Hg and stopcock  $S_2$  was opened only intermittently during the evacuation to remove sorbed gases from the sample. Then, with stopcock  $S_2$  closed the Hg was drained from the volumetric bulbs and the burette until the empty bulbs approximated the dead space and the volumetric portion of the apparatus was re-evacuated to remove any water vapor that entered the manifold from the moist sample during the first evacuation.

With stopcock  $S_2$  closed, He was introduced until the pressure of the volumetric portion of the apparatus was 736.2 mm. of Hg plus the previously measured water vapor pressure of the moist sample. The Hg in the left column of the manometer was then adjusted to a reference position in the 10 mm. tube section (Figure 1).

Stopcock  $S_2$  was then slowly opened to allow the gas to enter the sample flask. The initial pressure in the volu-

metric portion of the apparatus was re-established by displacing the gas in the volumetric bulbs with Hg from the Hg reservoirs. Final pressure adjustments were made by displacing the gas in the volumetric burette B. The initial pressure was attained when the Hg level in the left column of the manometer was again at the reference point. When the pressure remained constant for a period of time, the total volume of gas displaced from the volumetric bulbs and the burette was measured to 0.01 cc.

Water vapor in the sample flask was prevented from entering the volumetric section by opening stopcock  $S_2$  intermittently and for only short periods and by making the volume-pressure adjustment in such a manner that the gas was displaced from the volumetric bulbs into the sample flask.

This procedure was followed using He to determine the dead space. It was then repeated with the gas under study ( $O_2$  or  $CO_2$ ) and finally with He again. Precautions were taken each time to flush the lead tubes to the apparatus with the gas involved to remove the gas previously used. The volume of  $O_2$  or  $CO_2$  sorbed was found by subtracting the mean of the two dead space values from the value determined with these gases. This procedure of averaging dead space values determined before and after the gas sorption measurement was necessary because measurable quantities of water were

removed during the evacuations even though the intermittent evacuation method was used. Correction for the solubility of He in water was made when the dead space was calculated from the measurements using a value of  $11.0 \times 10^7$  at  $25^\circ \text{C}$ . for Henry's constant.

The volume of gas sorbed per 100 g. of  $110^\circ \text{C}$ . oven-dried soil was corrected to standard temperature and pressure conditions (S.T.P.).

#### Constant volume method

The sample and the volumetric portion of the apparatus were evacuated in the same manner as that described in the preceding section on the constant pressure method. Then with stopcock  $S_2$  closed the gas under study was introduced into the volumetric section until a pressure of approximately 200 mm. of Hg was obtained. The exact pressure of the gas in the system was recorded after the level of the Hg in the left arm of the manometer was adjusted to the reference point by means of the leveling bulb  $L_4$ . The Hg level in the left column of the manometer was lowered below the reference point and stopcock  $S_2$  was carefully opened to allow the gas to enter the sorption flask. When equilibrium was reached as indicated by no pressure change in the system, the Hg level in the manometer was readjusted to the reference point by the leveling bulb  $L_4$  and the pressure was recorded. This procedure

was repeated after known increments of gas were displaced from the volumetric bulbs by Hg. In each case, the gas in the sample flask after equilibrium was attained was calculated from the known initial volume of gas in the apparatus (known from previous calibration of the volumetric portion of the apparatus) and the measured change in pressure.

Helium was used to measure the dead space. In this case a dead space measurement was made before and after the series of  $O_2$  or  $CO_2$  measurements at different pressures. The amount of  $O_2$  or  $CO_2$  sorbed was calculated by subtracting the mean of the dead space values from the volume of  $O_2$  or  $CO_2$  in the sample flask at equilibrium.

Progressively higher equilibrium pressures were obtained when increments of gas were displaced from the volumetric bulbs. In this way the sorption of  $O_2$  and  $CO_2$  over a range of pressures was readily obtained.

The volume of the gas per 100 g. of  $110^{\circ}C$ . oven dried soil corrected to S.T.P. conditions was plotted against the equilibrium sorption pressure to obtain sorption isotherms.

The level of the Hg in the manometer was lowered below the reference point before stopcock  $S_2$  was opened to prevent the mass movement of water vapor from the sample flask into the volumetric section during the final pressure determina-

tion. If the Hg was not lowered, the Hg level in the left arm of the manometer rose above the reference point due to a decrease in total pressure since the pressure in the sample flask was less than it was in the volumetric section. Thus, the level of the Hg in the manometer had to be lowered from a position above the reference point to get the final equilibrium pressure measurement. In this lowering process, water vapor was drawn into the volumetric section.

### Soils and Clay Minerals

Soil samples for this investigation were obtained from the 0 to 6 inch depth in the Clarion, Edina, Ida, Lagonda, Luton and Webster soils, the 18 to 24 inch depth in the Clarion, Fayette and Zwingle series, and the 23 to 26 inch depth in the Edina soil. A sample of the Edina subsoil taken previously by Runkles (72) from the same location was also used in some experiments. The sample obtained by Runkles and the sample obtained later for this study will be referred to as Edina subsoil samples 1 and 2, respectively.

The clay minerals used in the investigation and their sources were vermiculite (Terra-Lite), Western Minerals Products; bentonite (Wyoming volclay bentonite), American Colloid Company; illite (Goose Lake grundite), Illinois Clay Products Company; and kaolinite (Peerless No. 2 Kaolin), R. T. Vanderbilt Company.

## Gases

The He gas was obtained from the Matheson Chemical Company, Joliet, Indiana, the O<sub>2</sub> from the Balbach Company, Omaha, Nebraska, and the CO<sub>2</sub> from the Pure Carbonic, Incorporated, Kansas City, Missouri. The gases were used directly from the cylinders, but they were passed through copper tubing in the constant temperature water bath to adjust their temperature.



## MOIST SOILS AND CLAY MINERALS

## Gas Sorption by Moist Soils and Clay Minerals

Soil and clay mineral samples were placed in the sample flask in a moist state and the quantity of  $O_2$  or  $CO_2$  sorbed was determined. The moist samples were then progressively dried to different moisture levels by evacuation at room temperature and the sorption measurements were repeated. The samples were finally dried in an oven at  $110^\circ C.$  for 48 hours and the final sorption measurements were made. After each period of drying, special precaution was taken to be sure that the temperature of the system was at  $25^\circ C.$  before the sorption values were determined.

The flask and the moist material were weighed together after each sorption measurement. The weights of the flask and the  $110^\circ C.$  oven-dried material were determined separately at the end of the drying sequence. The percent moisture in the sample at the time of each sorption measurement was then calculated on the basis of the weight of the  $110^\circ C.$  oven-dried material.

Only the Edina and Fayette subsoils were used in this study. Two of the experiments were carried out with Edina subsoil 1 which was air-dried at the time of sampling and stored in an air-dried state. The rest of the Edina subsoil

experiments were carried out with sample 2. This Edina subsoil sample and the Fayette subsoil were obtained at the same time and stored in the field moist condition. Except as specified later, the soil samples were used without treatment other than an alteration in moisture levels. In some instances the field moist soils were used as the initial moist sample, in others more water was added, and in some the soil was air-dried and then remoistened to the desired moisture level.

The bentonite, illite, and kaolinite clay minerals were originally air-dry. To obtain moist samples of these minerals that could be placed in the sample flask without puddling, the dry samples were sprayed with distilled water and mixed in a partially wetted state to form aggregates. The moist aggregates were then screened and the 1 to 2 mm. size fraction was used.

The vermiculite clay mineral, which was also originally air dry, was placed in an excess of water. Most of the excess water was then removed by filtering the material in a Buchner funnel under suction.

#### Oxygen sorption

The amount of  $O_2$  sorbed by samples of Edina and Fayette subsoils, kaolinite, vermiculite and bentonite at different moisture levels is shown in Figures 3, 4, 5, 6, 7 and 8. In

Figure 3. Oxygen sorbed by moist Edina subsoil sample 1. The solid line applies to the data obtained by Runkles (72) and to trial 1

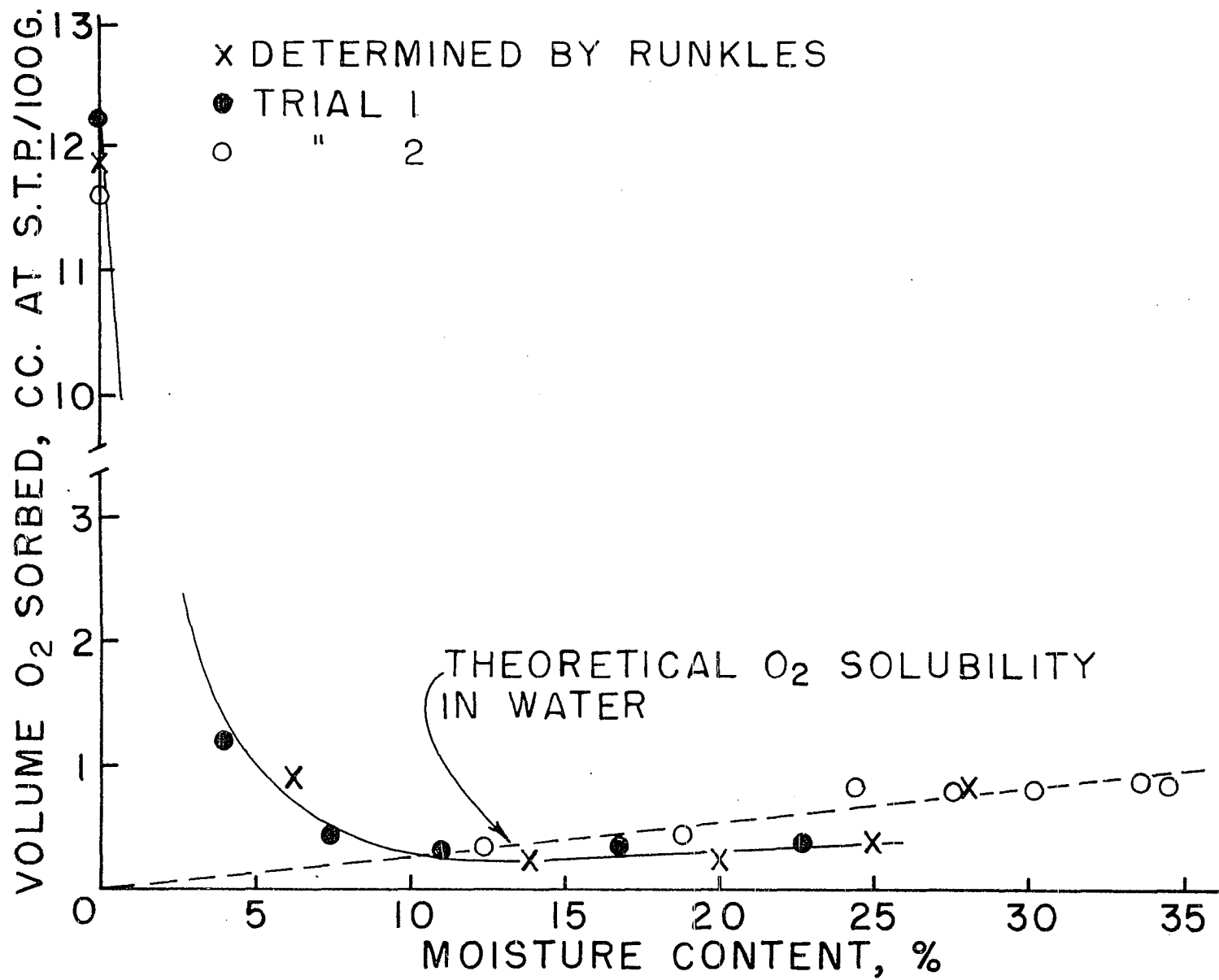


Figure 4. Oxygen sorbed by moist Edina subsoil sample 2. The soil was field moist in trial 1, air-dried and remoistened in trials 2, 3 and 4, and oven-dried and remoistened in trial 5. Values obtained from sorption isotherms are indicated by a diagonal line (/) through the point

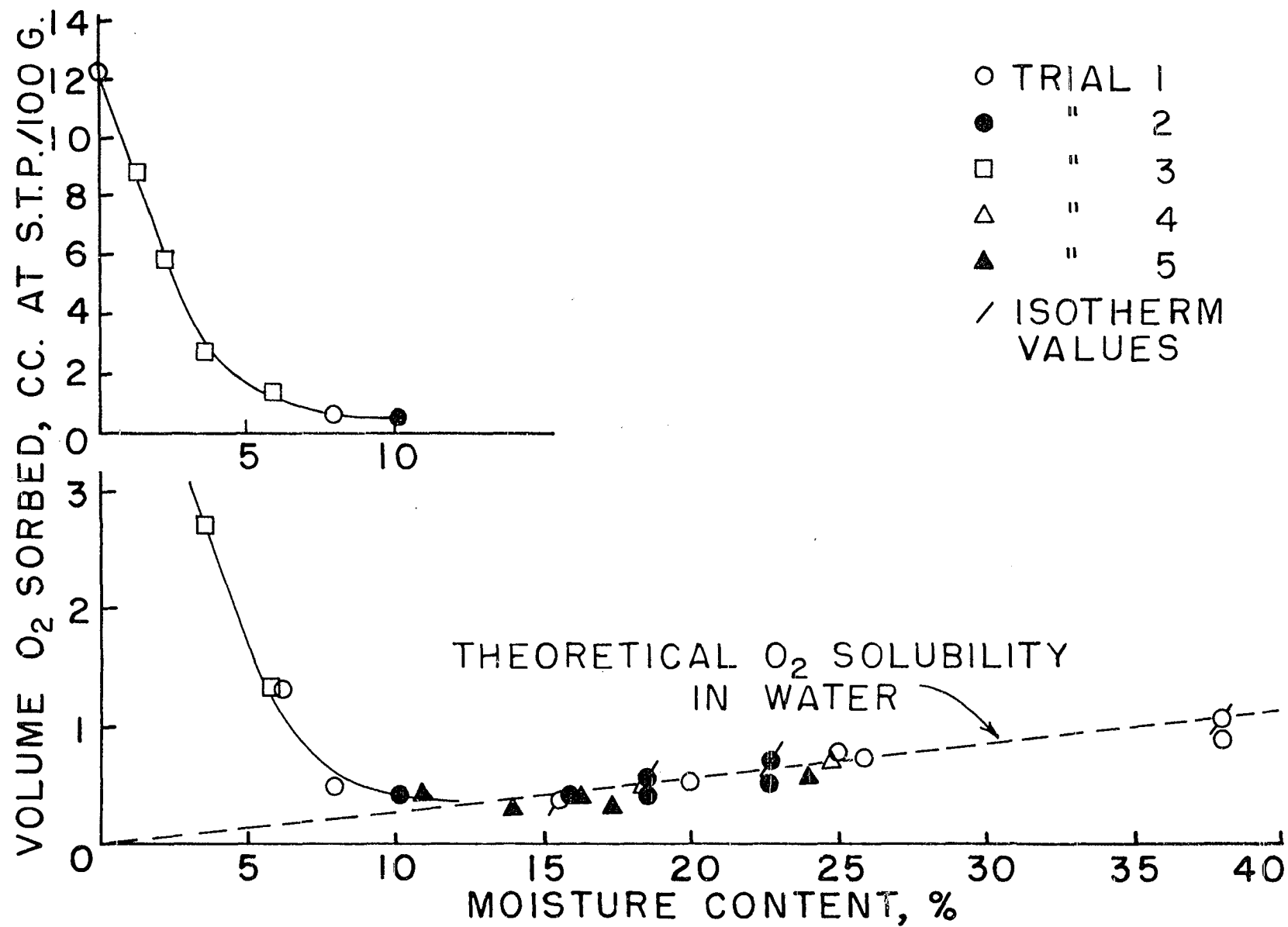


Figure 5. Oxygen sorbed by moist Fayette subsoil. Field moist soil with added water was used in each trial

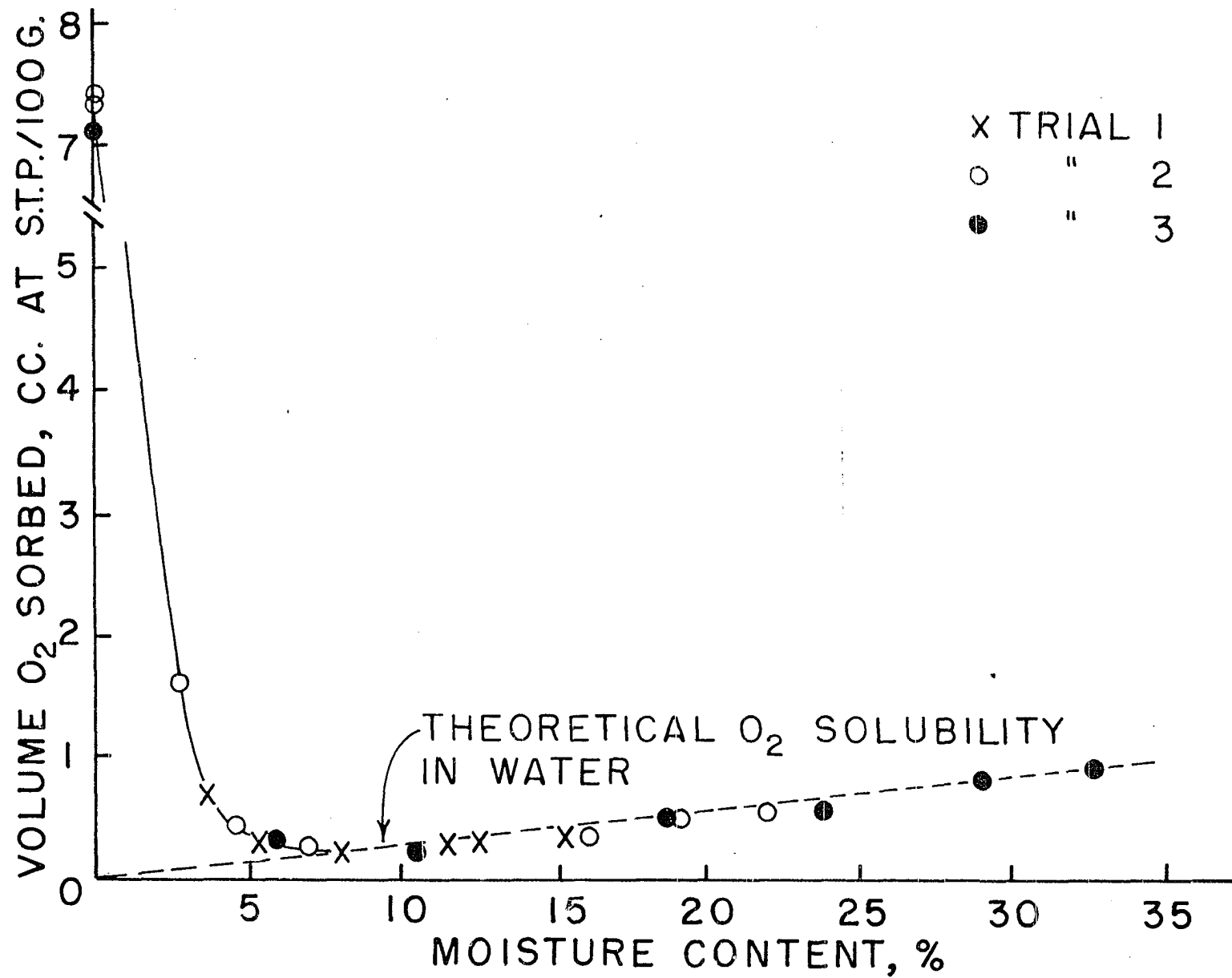




Figure 6. Oxygen sorbed by moist kaolinite

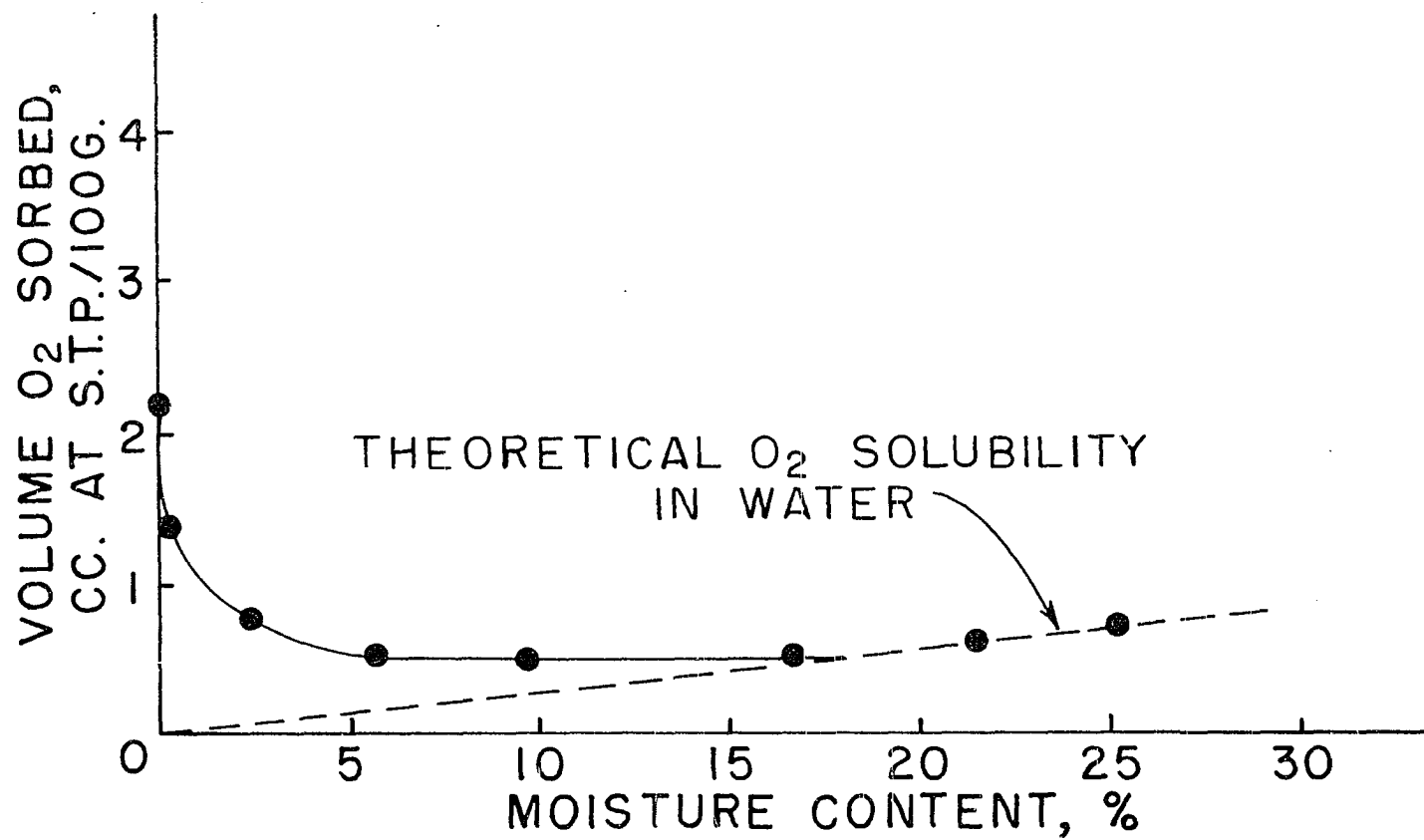


Figure 7. Oxygen sorbed by moist vermiculite

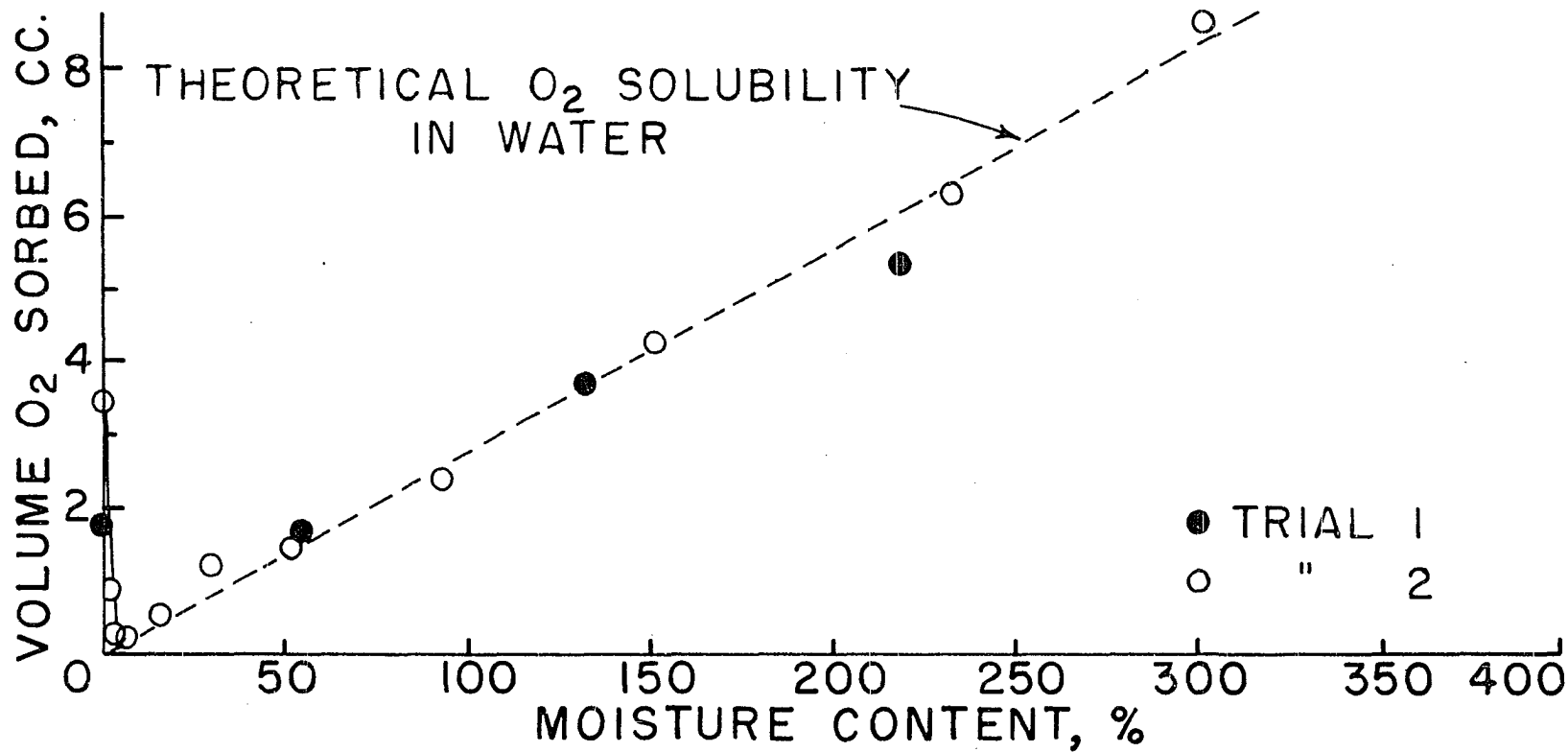
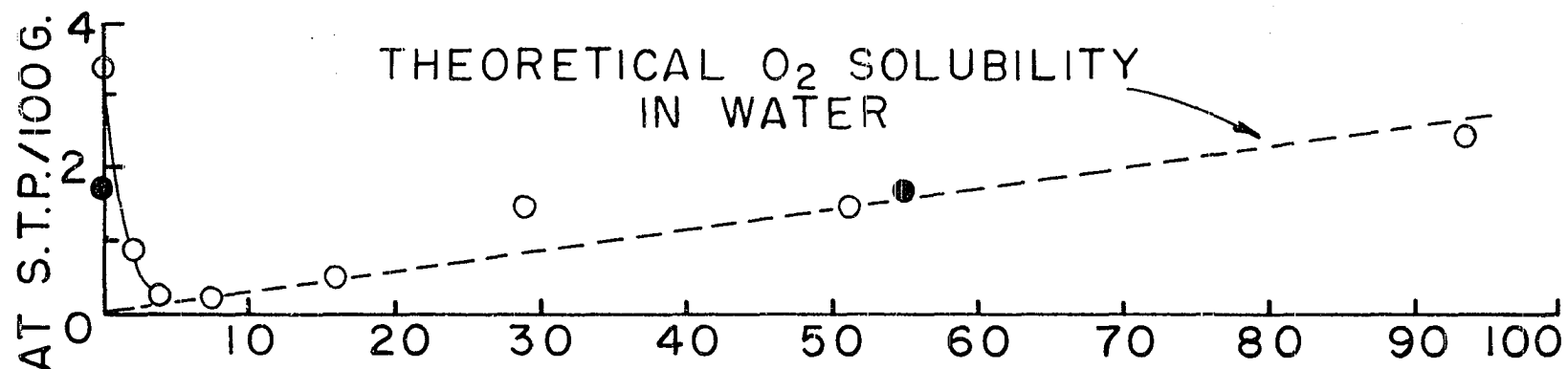
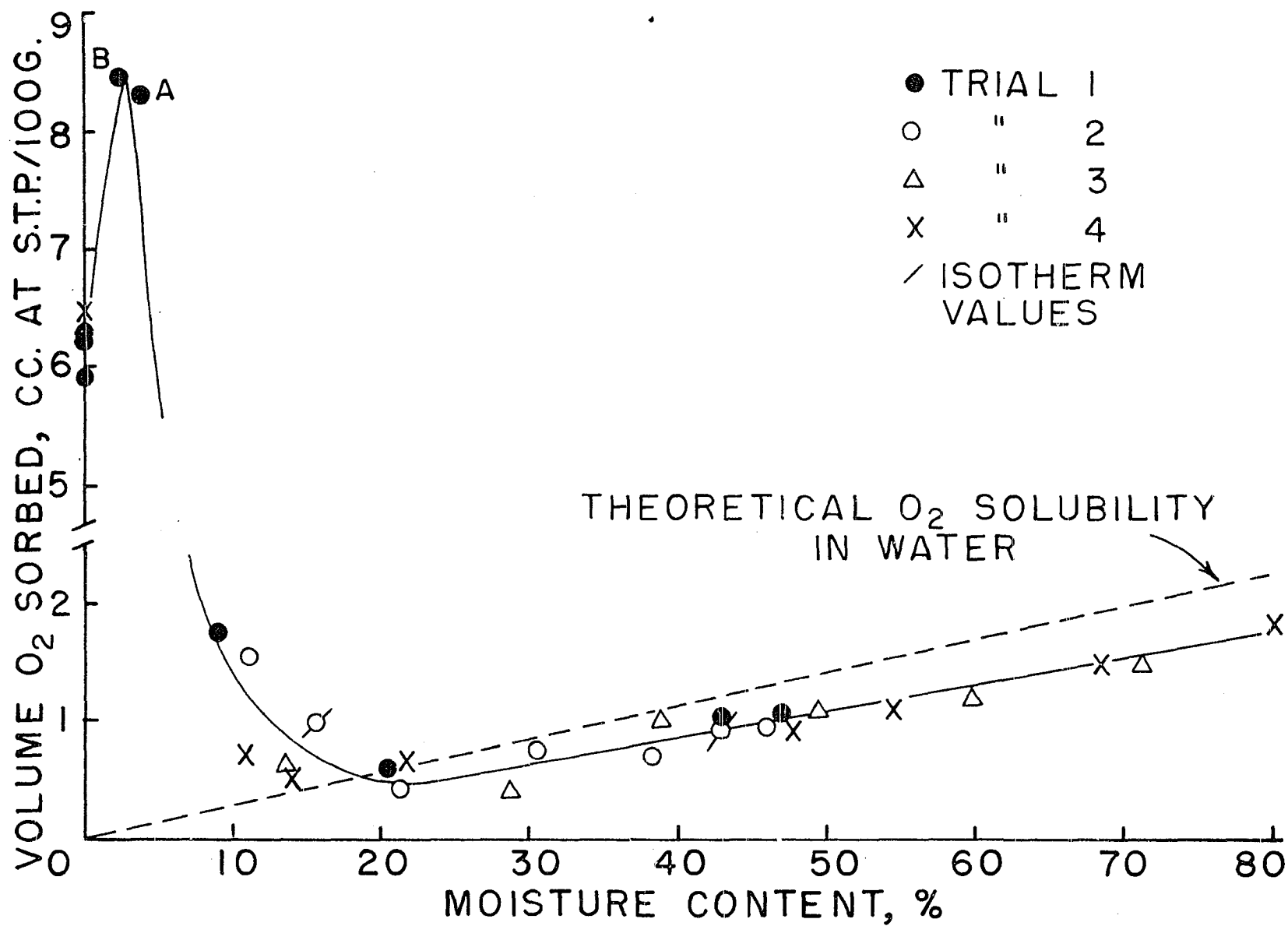


Figure 8. Oxygen sorbed by moist bentonite. Points A and B represent un-equilibrated determinations after 122 and 144 hours, respectively. Values obtained from sorption isotherms are indicated by a diagonal line (/) through the point



these graphs, the volume of  $O_2$  at standard temperature and pressure (S.T.P.) sorbed per 100 g. of material ( $110^\circ C.$  oven-dried basis) has been plotted against the percent moisture in the sample. The sorption measurements were carried out at  $25^\circ C.$  and an  $O_2$  partial pressure of 732.6 mm. of Hg. Since the percent moisture is based on the  $110^\circ C.$  oven-dried weight of the sample, the values on the abscissa of these graphs also indicate the grams of water associated with the 100 g. of material whose sorption is shown on the ordinate.

Assuming that the water in these moist samples was not affected by the presence of the soil or clay mineral materials, the theoretical solubility of  $O_2$  in the water was calculated using the value of  $3.24 \times 10^7$  for Henry's constant (43, p. 1480). The theoretical amount of  $O_2$  that could dissolve in an equivalent amount of water to that in the moist samples is shown by a dashed line in each graph. The effect of the soils and clay minerals on the solubility of  $O_2$  in water can thus be observed by comparing the experimentally determined sorption points with this theoretical solubility curve at the same moisture level.

The results shown in Figure 3 were obtained with Edina subsoil sample 1. Runkles (72) also used this sample. Thus, for comparative purposes, the  $O_2$  sorption values reported by

him have been included in this figure. This Edina sample was initially air-dry, therefore it was moistened prior to each sorption experiment.

In trial 1 and in Runkles' experiment the soil was moistened to about 25% moisture. In both cases the amount of  $O_2$  sorbed by the Edina subsoil containing 20 to 25% moisture was less than the amount that could theoretically dissolve in the water present if the water behaved as pure water. In trial 2 a portion of the same soil sample was moistened to approximately 35% moisture. In this case the  $O_2$  sorption values were about the same as the theoretical solubility of  $O_2$  in pure water at all moisture levels above 12%. Unfortunately the supply of Edina subsoil sample 1 was then depleted and further trials to reconcile the difference in results obtained in the two trials was impossible. This point will be discussed, however, after additional data obtained with another moist Edina subsoil sample and moist bentonite have been considered.

The  $O_2$  sorbed by moist Edina subsoil sample 2 is shown in Figure 4. In this case the sorption experiments were repeated with different portions of the soil that had received different initial moisture treatments. In trial 1 the field moist soil was used without treatment. The soil was air-dried at the time of sampling and stored in an air-dried state for



this increase was due to capillary forces which increased the solubility of  $O_2$  in water. Most of the increase and particularly that occurring near the oven-dry state was due to an increase in physical adsorption of  $O_2$  as water was removed and more adsorption sites became accessible.

The  $O_2$  sorption values obtained for moist Fayette subsoil and kaolinite (Figures 5 and 6) were similar to those obtained for moist Edina subsoil sample 2. In the moist range the amount of  $O_2$  sorbed was essentially the same as the theoretical solubility of  $O_2$  in pure water. In the dry range there was a rapid and continuous increase in sorption as the water content was decreased.

The amount of  $O_2$  sorbed by moist vermiculite (Figure 7) was also comparable to the theoretical solubility of  $O_2$  at the higher moisture levels. In the case of vermiculite, however, no large increase in sorption occurred as the last increments of water were removed. Apparently the surface area available for  $O_2$  adsorption in the absence of water was relatively small in the vermiculite compared to the soils. Vermiculite is an expanding 2:1 type clay mineral, but at the low moisture levels the lattice would be contracted. Under these conditions it is expected that the internal surface of the vermiculite was probably not accessible for the adsorption of  $O_2$ . In this event the physical adsorption of

O<sub>2</sub> by dry vermiculite was limited to the external surface, but this surface was relatively small because the material used was a coarse exfoliated commercial product.

Moist bentonite (Figure 8) exhibited a different type of O<sub>2</sub> sorption behavior than the other materials previously discussed. Even at a moisture level of 80% the amount of O<sub>2</sub> sorbed was less than the theoretical solubility of O<sub>2</sub> in pure water. This behavior is similar to that observed in trial 1 with Edina subsoil sample 1 (Figure 3). In both cases, it is believed that the originally air-dry sample did not expand enough upon moistening for the water between the lattice plates to be available for the solution of O<sub>2</sub>. The observation that the Edina subsoil sorption values were equal to the theoretical solubility values when the soil was moistened to a high moisture level supports this idea, but bentonite moistened to 80% still gave low O<sub>2</sub> sorption values.

In the dry range, O<sub>2</sub> sorption values increased to high, but uncertain values and then decreased as the moisture content was decreased. These results are comparable to those reported by Brooks (13) and Escard (22, 23). According to these investigators, some of the internal surfaces of the clay mineral may be accessible for a non-polar gas when water is first removed. The amount of gas sorbed thus increases rapidly as the water is removed from between the

plates. When more water is removed, however, the lattice layers contract and the internal surfaces are no longer accessible for non-polar gas adsorption. The amount of gas sorbed is then decreased by the removal of water.

Kaolinite (Figure 6), which is a non-expanding clay mineral, did not exhibit this discontinuity in  $O_2$  sorption when water was removed. The Edina subsoil (Figures 3 and 4) and the Fayette (Figure 5) did not show this discontinuity either, even though they contain an expanding lattice montmorillonite type clay mineral. This would indicate that the interlayer surfaces of dehydrated soil clays remain accessible for the adsorption of  $O_2$  whereas those in bentonite do not. It is possible that this may be due to the presence of organic materials between the plates of the soil clay mineral which prevent the contraction of the clay lattice. As a result, the amount of  $O_2$  adsorbed by Fayette (7 cc./100g.) and Edina (12 cc./100 g.) subsoils was greater than that adsorbed by bentonite (6 cc./100 g.) in the oven-dried state. These results emphasize that soil clays may not behave like comparable clay minerals from natural clay deposits.

An attempt was made also to determine the amount of  $O_2$  sorbed by moist illite and Webster surface soil samples, but an equilibrium state could not be reached. A comparison of the non-equilibrated sorption values with the solubility

data of  $O_2$  in pure water indicated that the  $O_2$  sorbed was much greater than the theoretical solubility of  $O_2$  in the water even at the high moisture levels. These high sorption values were probably due to microbial consumption since these materials contained large amounts of organic matter.

In the course of this investigation,  $O_2$  sorption isotherms were determined for moist Edina subsoil sample 2 and for moist bentonite. These isotherms are shown in Figure 9. The  $O_2$  sorption values shown in Figure 4 and 8 by a slanted line (/) through the points were obtained from these adsorption isotherms. These  $O_2$  sorption values should be more reliable than the single sorption measurements at a pressure of 736.2 mm. of Hg since several determinations were made for each sorption isotherm.

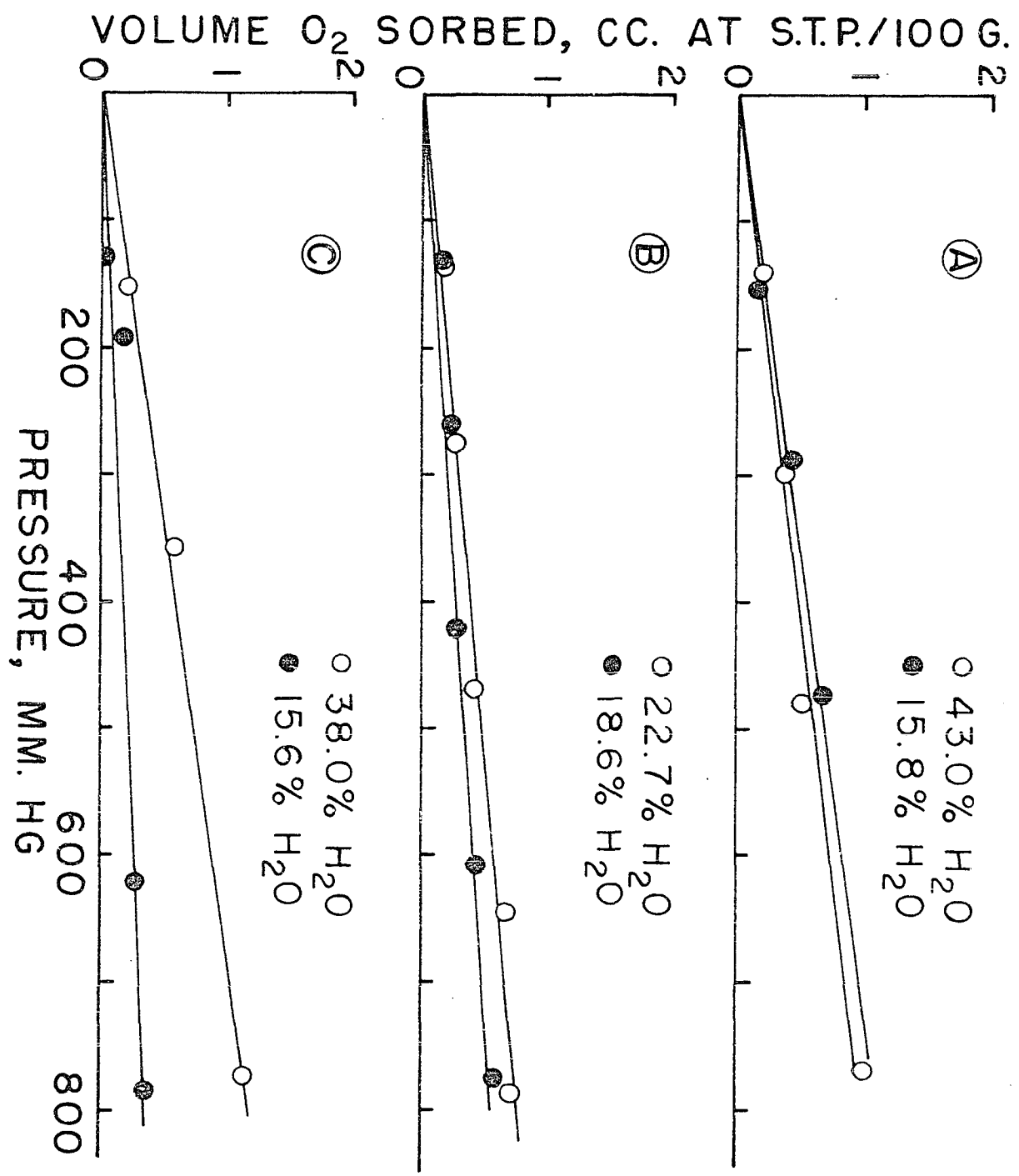
The sorption isotherms for the moist Edina subsoil and bentonite samples exhibited a linear relationship between the amount of  $O_2$  sorbed and the partial pressure of  $O_2$ . This relationship is comparable to the linear relationship between the solubility of  $O_2$  in water and the partial pressure of  $O_2$  predicted by Henry's law. It was therefore possible to determine if the water in these moist samples behaved like pure water at a particular moisture level by comparing the proportionality constant from the isotherms with Henry's law constant for pure water. The conclusions from

Figure 9. Oxygen sorption isotherms for bentonite and Edina subsoils at different moisture levels.

A. Bentonite

B. Edina subsoil sample 2, air-dried and remoistened

C. " " " ", field moist condition



this comparison, however, were the same as those based on changes in  $O_2$  sorption with changes in moisture content which have been presented earlier.

#### Carbon dioxide sorption

Preliminary investigations were conducted on the sorption of  $CO_2$  by moist materials because  $CO_2$  is more polar and has a greater solubility in water than  $O_2$ . In these experiments  $CO_2$  sorption isotherms were determined and the  $CO_2$  sorption values at a specific pressure were taken from the isotherms. Large volumes of  $CO_2$  were sorbed by the moist materials as was expected, but the equilibration time was long when high partial pressures of  $CO_2$  were used. Therefore, in most cases the sorption measurements were made with  $CO_2$  partial pressures below 100 mm. of Hg.

Moist samples of vermiculite, kaolinite, illite and Edina subsoil sample 2 were progressively dried as in the  $O_2$  sorption experiments and the volume of  $CO_2$  sorbed at the different moisture levels determined. The amount of  $CO_2$  sorbed by these materials at a  $CO_2$  partial pressure of 76 mm. of Hg is shown in Figures 10, 11 and 12. The theoretical solubility of  $CO_2$  in an equivalent amount of pure water was calculated using Henry's constant of  $0.124 \times 10^7$  (43, p. 1480) and plotted in these graphs also.

Figure 10. Carbon dioxide sorbed by moist vermiculite and kaolinite



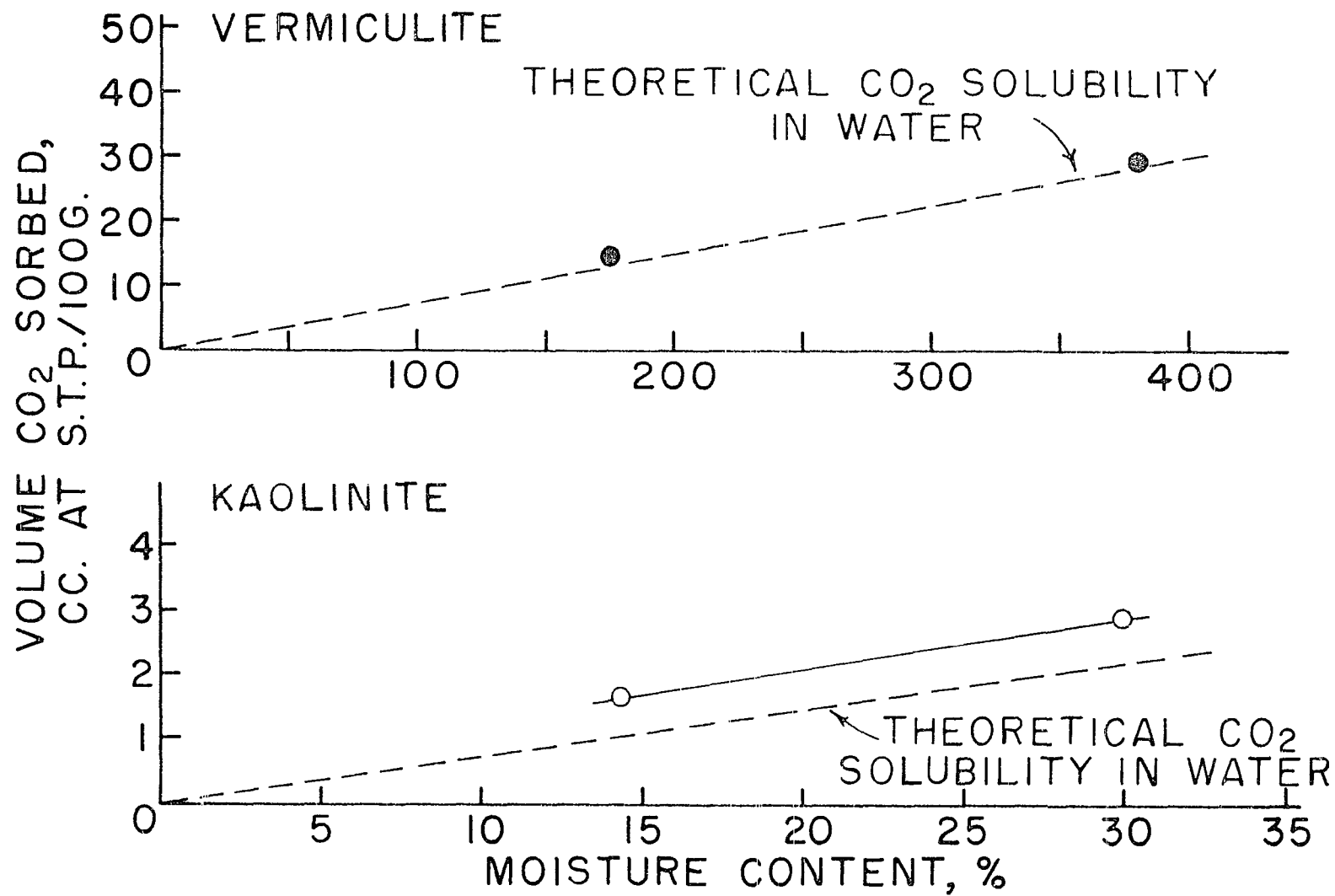


Figure 11. Carbon dioxide sorbed by moist Edina subsoil sample 2. The soil was field moist in trial 1, air-dried and remoistened in trials 2 and 3

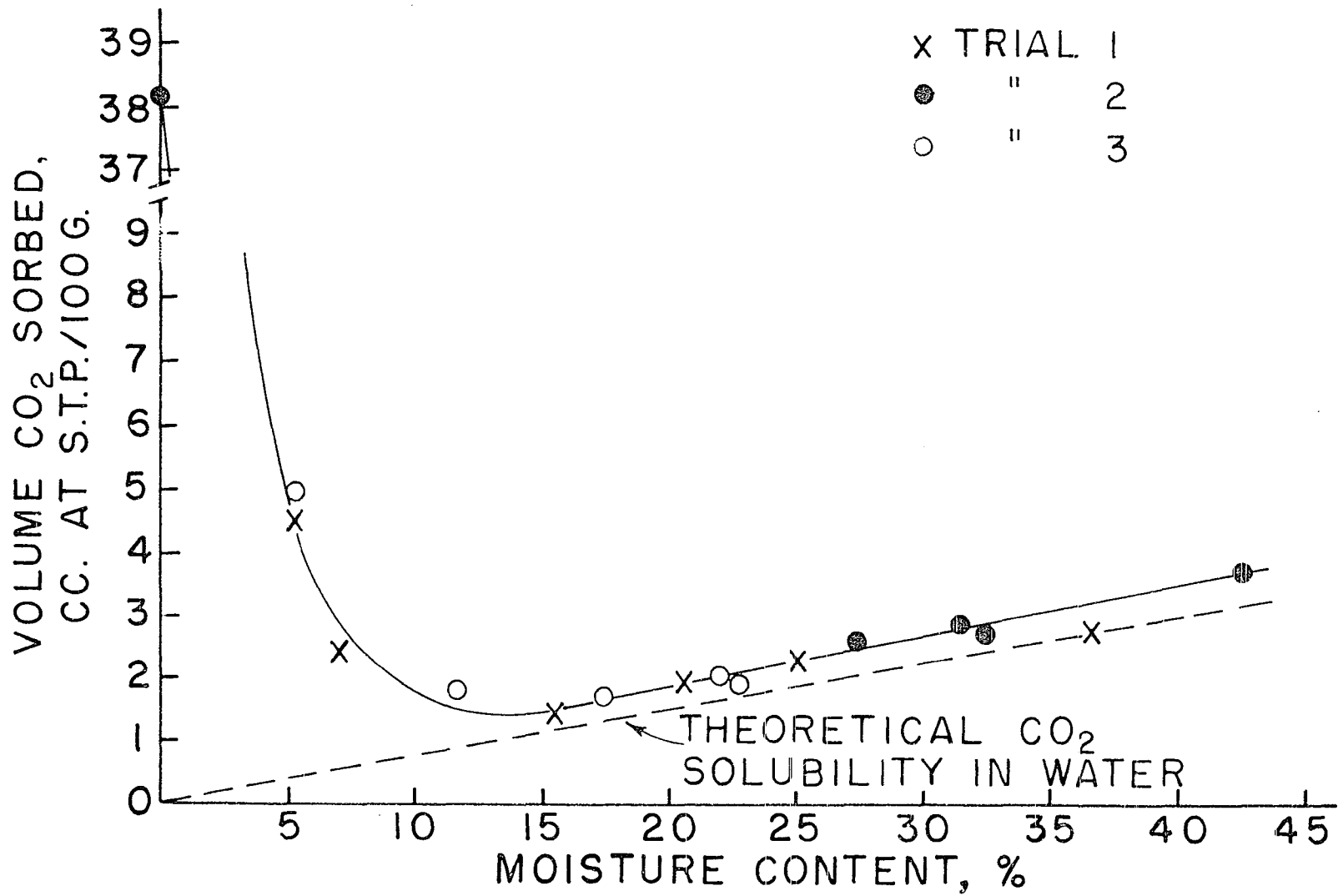
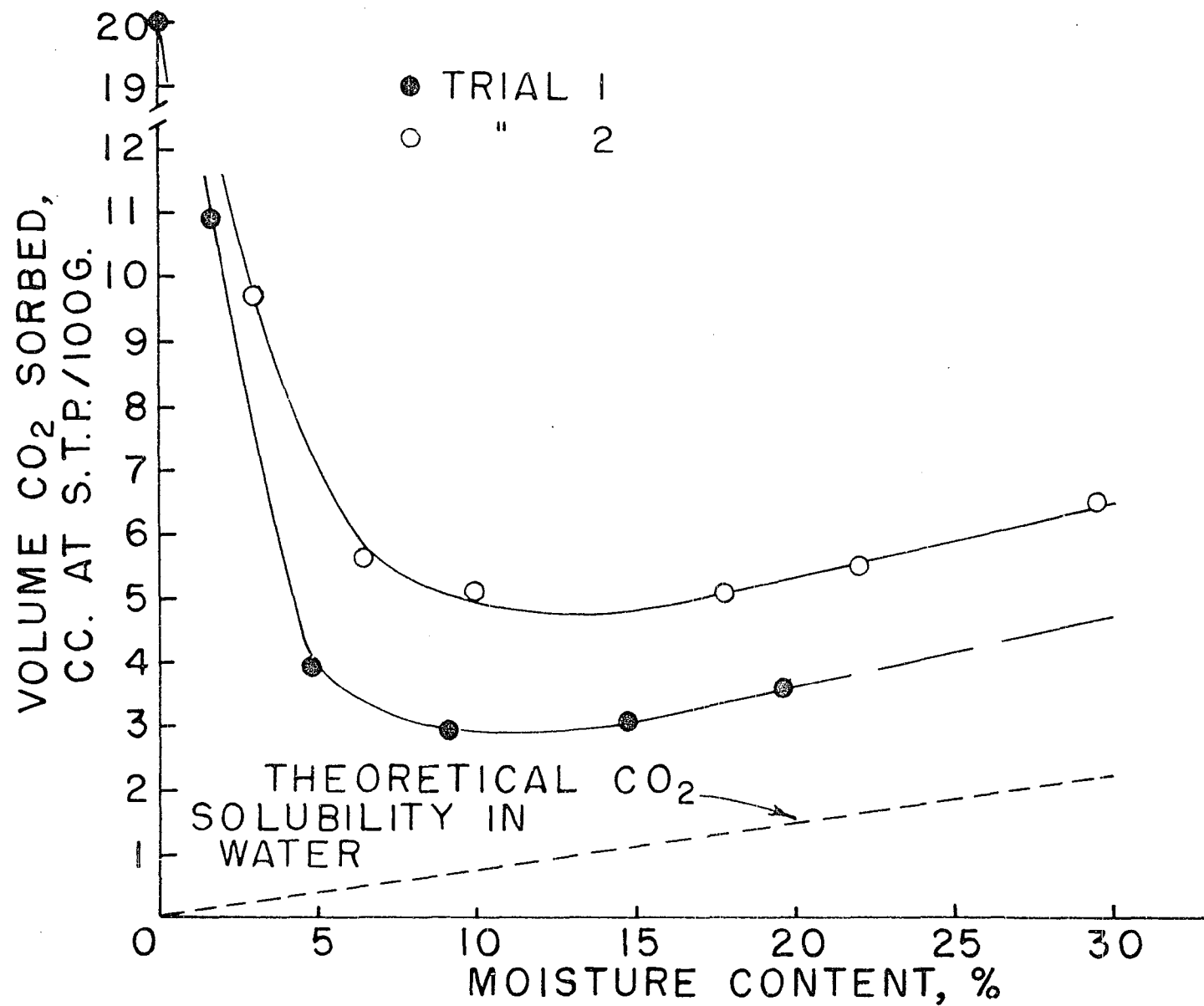


Figure 12. Carbon dioxide sorbed by moist illite



The volume of  $\text{CO}_2$  sorbed by moist vermiculite was essentially equal to the theoretical solubility of  $\text{CO}_2$  in the water present if that water behaved as pure water. The  $\text{CO}_2$  sorption values for kaolinite (Figure 10) and Edina subsoil (Figure 11) at the higher moisture levels were slightly higher than the theoretical solubility values. When water was removed from these samples, however, the amount of  $\text{CO}_2$  sorbed decreased in the same proportion as the theoretical  $\text{CO}_2$  solubility. It is apparent that part of the total  $\text{CO}_2$  sorbed is due to the solution of  $\text{CO}_2$  in the water. Call (16) and Wade (82) obtained sorption values for ethylene dibromide in soils which were higher than the theoretical solubility curve at high moisture levels. Their experimental curves were also parallel to the theoretical solubility curve.

In trial 1 of the Edina subsoil experiments, field moist soil was used. In trials 2 and 3, the soil was air-dried and remoistened to different moisture levels prior to the sorption measurements. Comparable results were obtained in the three trials, however, indicating that there was no effect from the initial moisture treatment and that it was possible to obtain reproducible  $\text{CO}_2$  sorption values from one trial to another with this material.

Below 15% moisture content, the amount of  $\text{CO}_2$  sorbed by Edina subsoil increased rapidly when the water was removed.

This increase like that of  $O_2$  was due to the effect of capillary forces and an increase in the accessibility of the adsorption sites for the gas molecules.

Moist illite (Figure 12) sorbed more  $CO_2$  than that which could be accounted for by the solubility of  $CO_2$  in the water present. The illite used in trials 1 and 2 was moistened to slightly different moisture levels. The amounts of  $CO_2$  sorbed by the two samples of illite, however, are quite different. Again the experimental sorption curves were nearly parallel to the theoretical solubility curve at moisture levels above 15%. Below 15% moisture content, the amount of  $CO_2$  sorbed increased rapidly as the water was removed and the difference between the two samples decreased.

Carbon dioxide sorption measurements were attempted with moist bentonite, but equilibrium could not be obtained even at low partial pressures of  $CO_2$ . The unequilibrated values observed, however, were much higher than the theoretical solubility values.

High  $CO_2$  sorption values could occur because of a neutralization reaction between  $CO_2$  and dissolved bases in the moist samples. The pH values for all of the materials were therefore determined using a 2:1 mixture of water and soil or clay mineral. The results are given in Table 4.

Table 4. pH values of soils and clay minerals

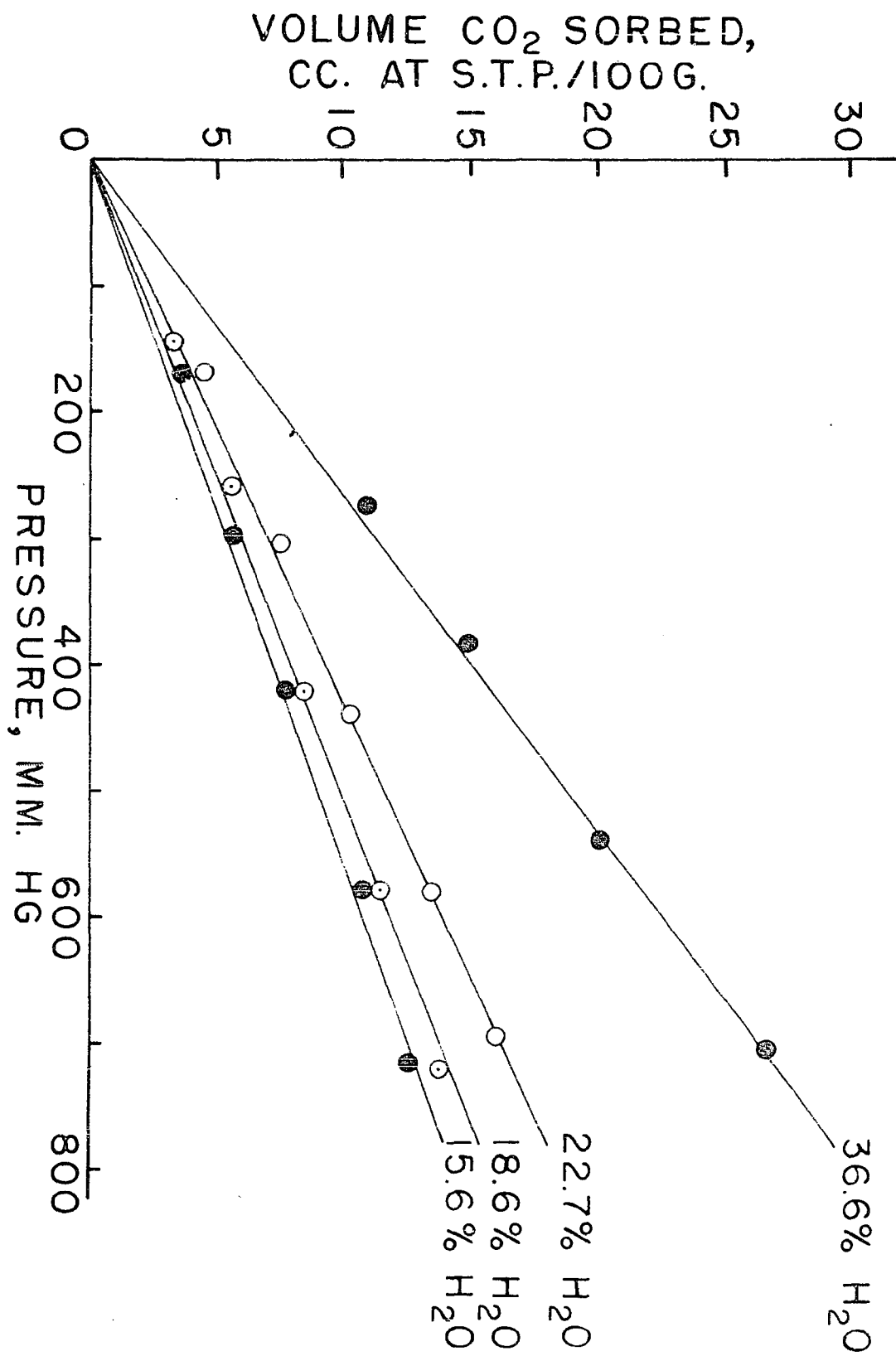
| Material      | pH   |
|---------------|------|
| Edina subsoil | 4.97 |
| Bentonite     | 8.40 |
| Illite        | 7.16 |
| Kaolinite     | 4.25 |
| Vermiculite   | 6.02 |

The pH values indicate that the high CO<sub>2</sub> sorption values of kaolinite and Edina subsoil at least are not due to an acid-base neutralization reaction. It is possible with bentonite, on the other hand, that neutralization may have occurred. The reason for the high CO<sub>2</sub> sorption values was not investigated further.

The CO<sub>2</sub> sorption values reported in Figures 10, 11 and 12 were obtained from sorption isotherms that were determined with CO<sub>2</sub> partial pressures of less than 100 mm. of Hg. Sorption isotherms with CO<sub>2</sub> partial pressures that exceeded 700 mm. of Hg were also determined, however, to characterize the shape of the isotherms. The isotherms obtained with moist Edina subsoil sample 2 that was adjusted to different moisture levels are shown in Figure 13. These linear sorption isotherms are typical of those found with all moist materials at the high moisture levels and with CO<sub>2</sub> partial pressures up to 100 or 700 mm. of Hg.



Figure 13. Carbon dioxide sorption isotherms for moist Edina subsoil sample 2



## Vapor Pressure of Water in Moist Soils and Clay Minerals

In sorption measurements with moist samples, water vapor contributed to the total gas pressure in the sorption apparatus. To determine  $O_2$  or  $CO_2$  sorption at a specified partial pressure of the gas the vapor pressure of water was required. Therefore, prior to the sorption measurements at each moisture level the vapor pressure of water in the sample was determined as described in the section on methods.

The results of these vapor pressure measurements are presented in Figures 14, 15, 16, 17, 18 and 19 for Edina subsoil 2, Fayette subsoil, illite, kaolinite, vermiculite and bentonite samples, respectively. In these figures the vapor pressure values have been plotted against the moisture content of the sample at the time the measurements were made. The vapor pressure of pure water at  $25^{\circ}C$ . is 23.8 mm. of Hg. All of the materials exhibited vapor pressures of this magnitude at the high moisture levels. When water was gradually removed from the moist samples, the vapor pressure decreased in all cases, but the materials differed in the moisture level at which the decrease occurred and in the rate of decrease.

The method for measuring the vapor pressure was not sensitive enough to indicate the moisture level at which the

Figure 14. Water vapor pressure of moist Edina subsoil sample 2 at different moisture contents

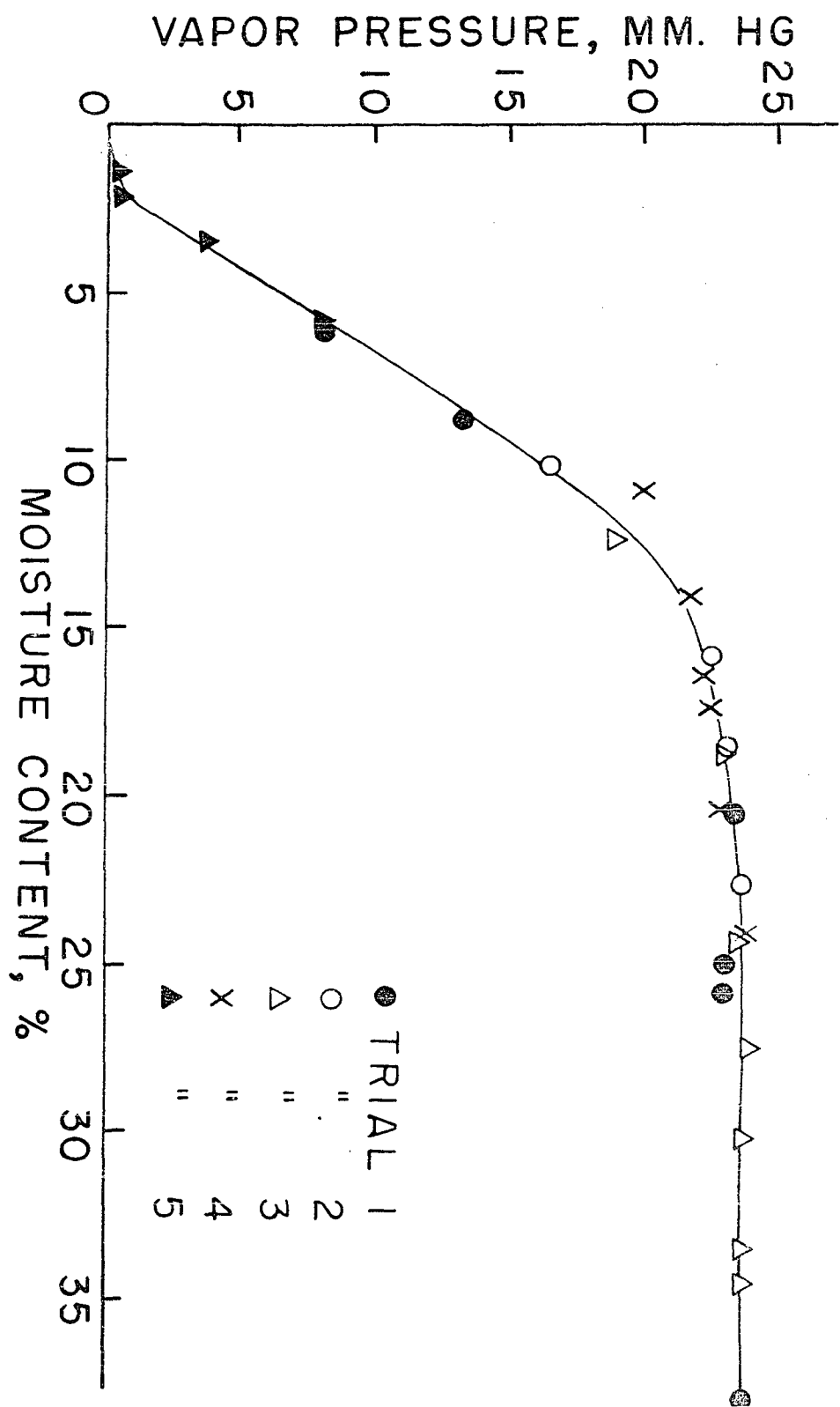


Figure 15. Water vapor pressure of moist Fayette subsoil at different moisture contents

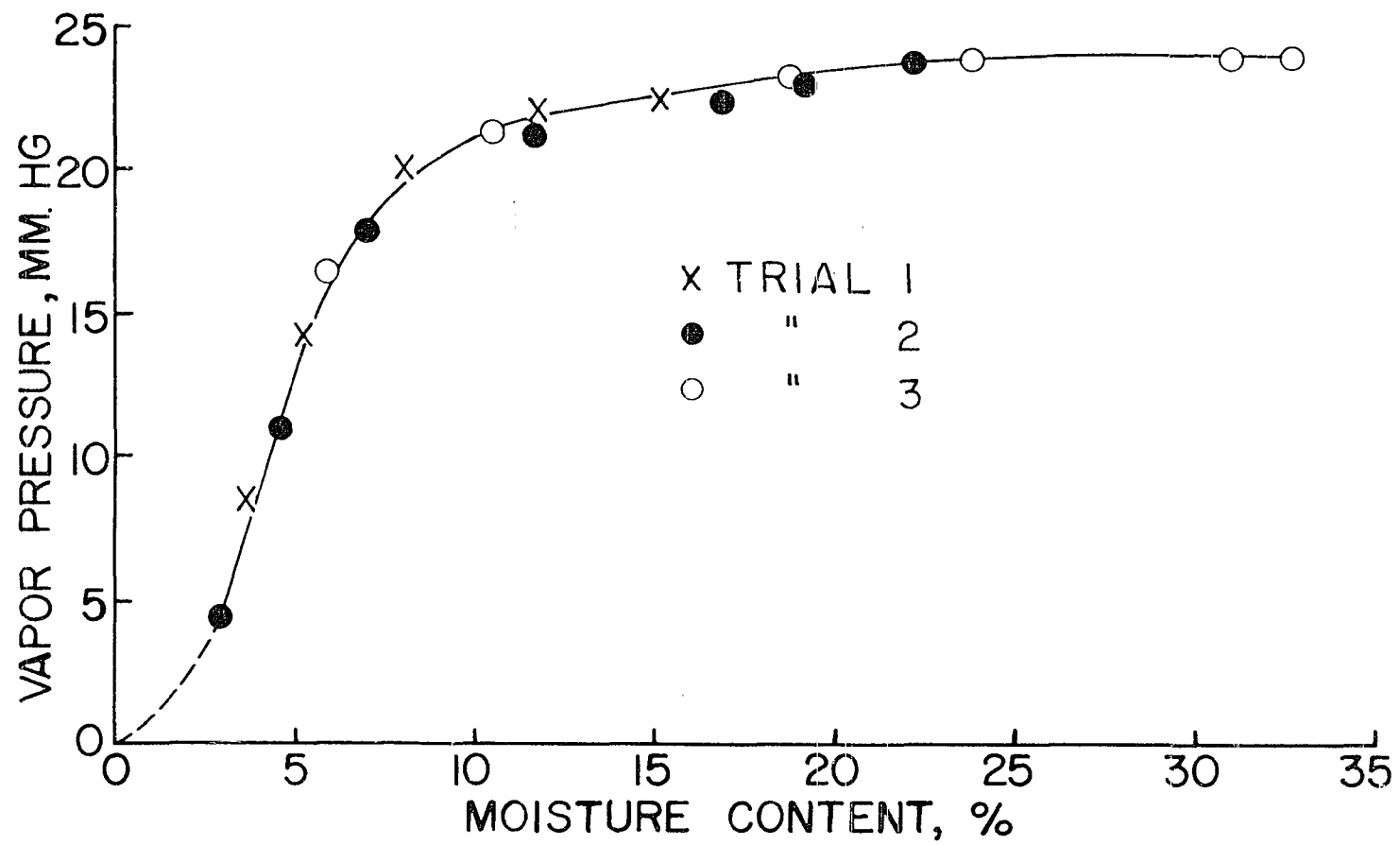


Figure 16. Water vapor pressure of moist illite at different moisture contents



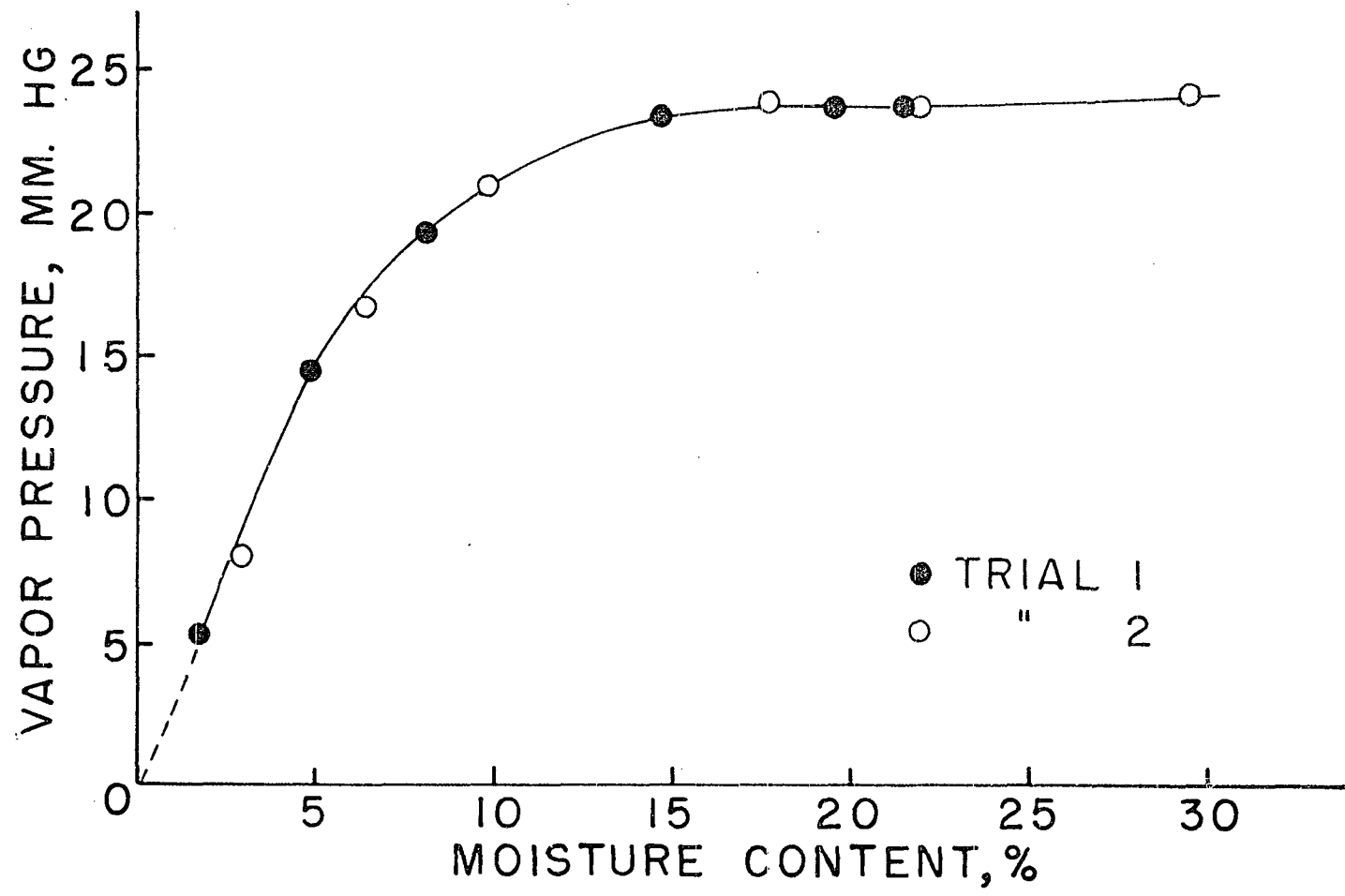


Figure 17. Water vapor pressure of moist kaolinite at different moisture contents

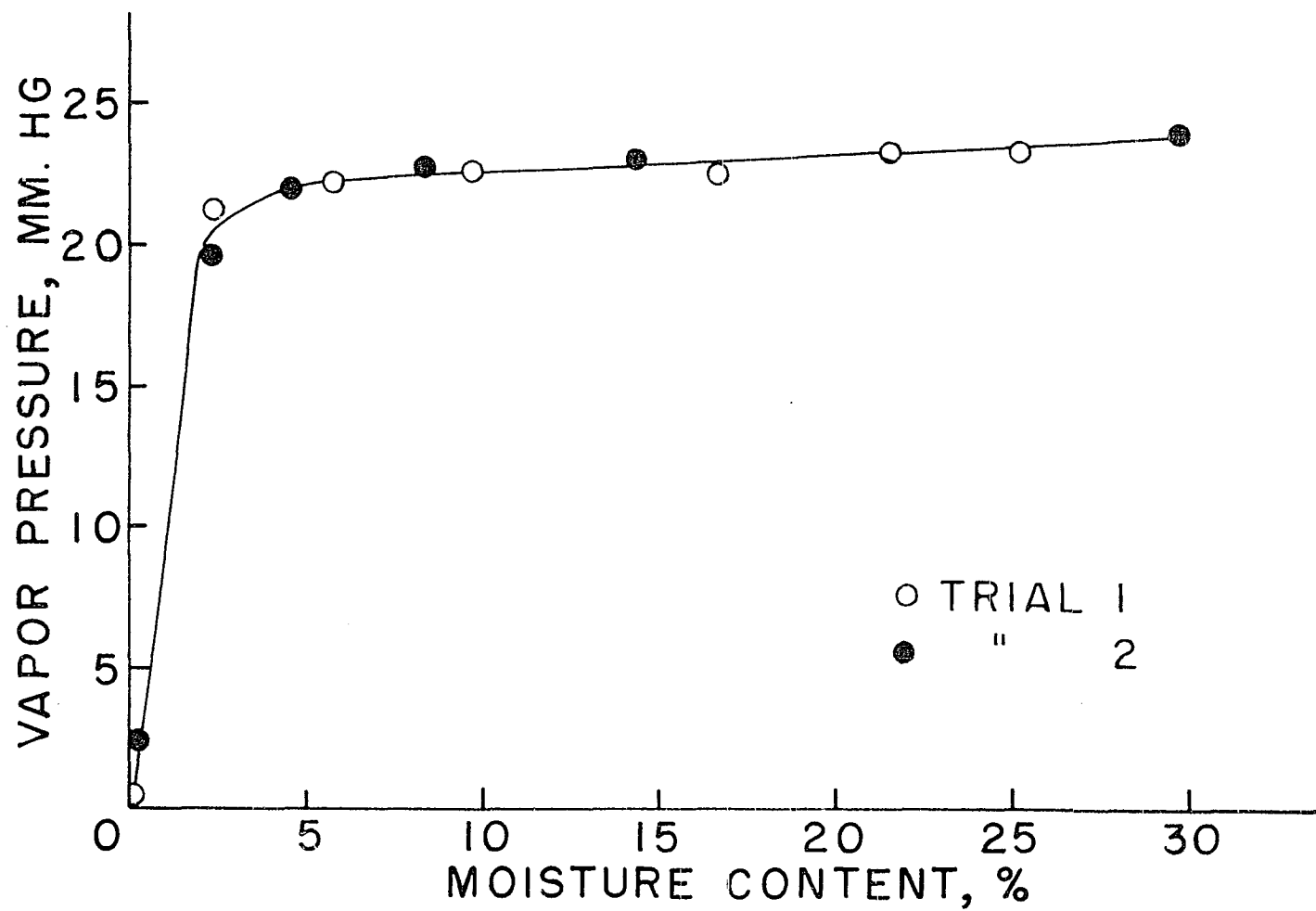


Figure 18. Water vapor pressure of moist vermiculite at different moisture contents

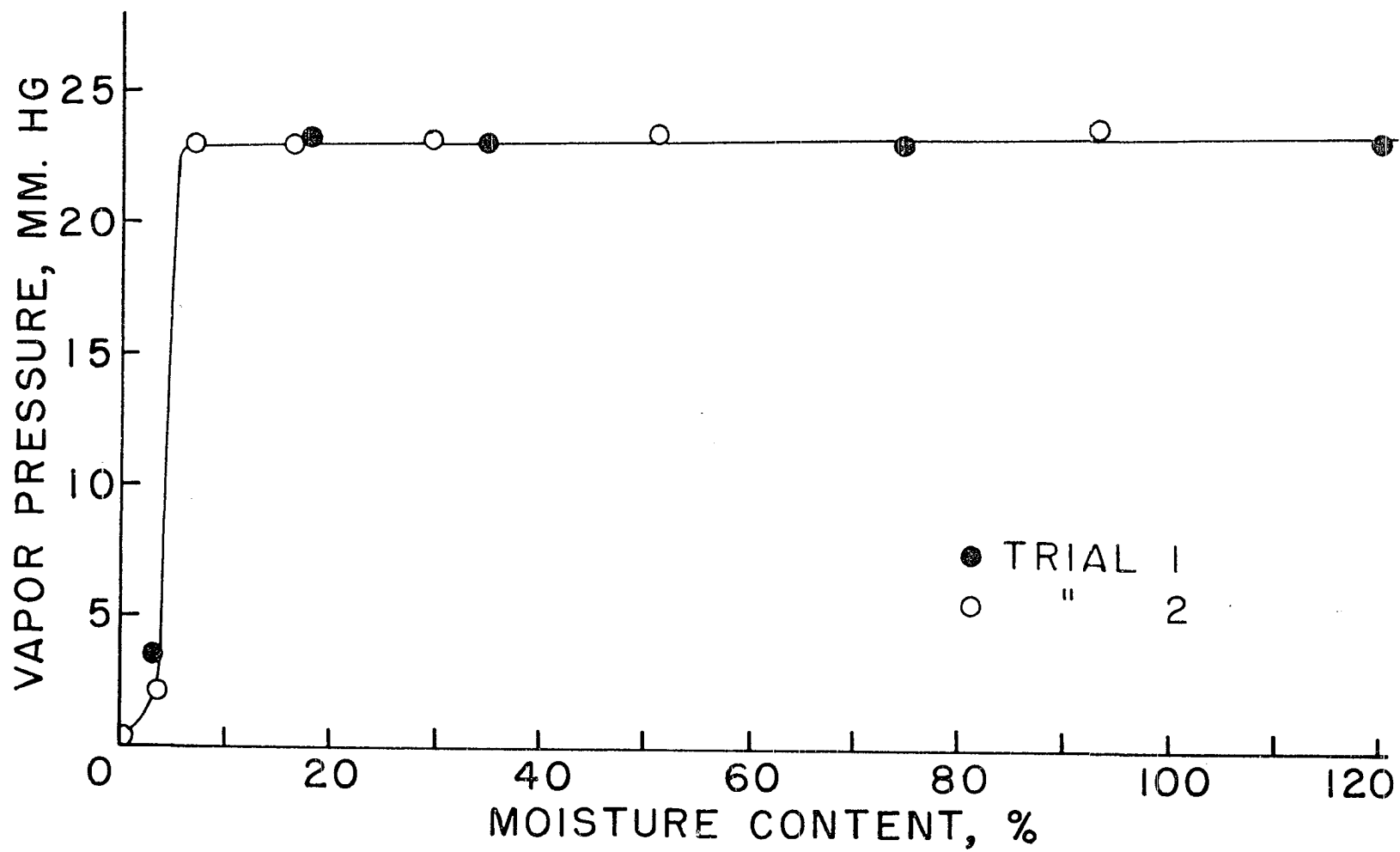
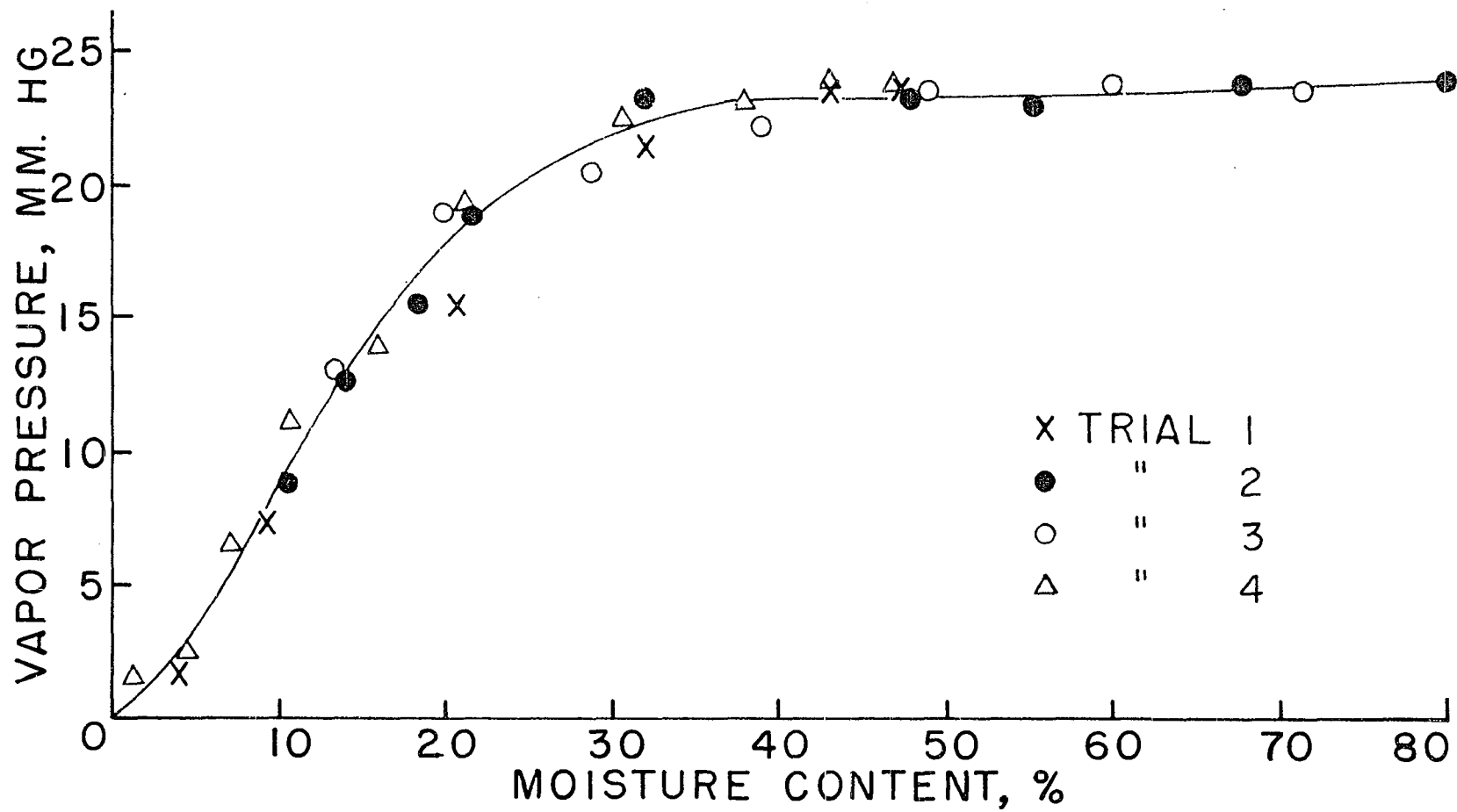


Figure 19. Water vapor pressure of moist bentonite at different moisture contents



first small decrease in vapor pressure occurred. The point at which a relatively large decrease in vapor pressure occurred can be readily seen from the graphs. This decrease occurred in the soils and illite at about 15%, whereas in the bentonite the moisture content was approximately 40%. Kaolinite and vermiculite, on the other hand, exhibited a sharp drop in vapor pressure at about 5% moisture content.

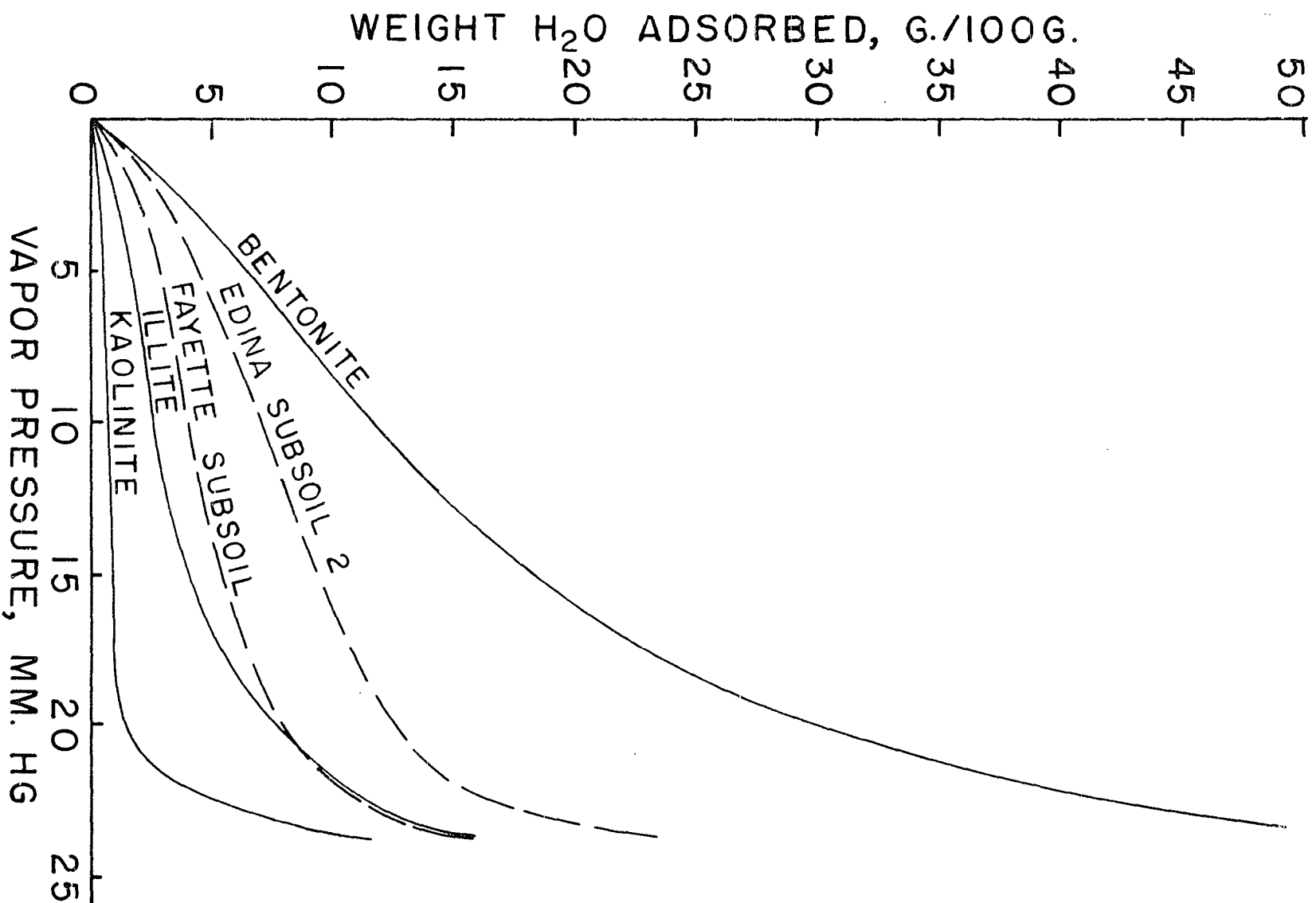
The sharp decrease in vapor pressure and the sharp increase in gas sorption by the moist materials occurred at approximately the same moisture level. In the next section, gas sorption values have been calculated on the basis that the initial decrease in vapor pressure was entirely due to capillary effects. These calculated sorption values are comparable to the experimentally determined values. This would indicate that the initial decrease in vapor pressure noted in these curves is primarily due to capillary effects and not the result of ion and clay surface hydration.

To obtain a better comparison of the materials, the vapor pressure results have been combined in Figure 20. Furthermore, since the method used in obtaining these vapor pressure-moisture content measurements could be used to determine desorption isotherms, the results have been presented in Figure 20 in the usual desorption isotherm form.

The water desorption isotherms are similar in shape



Figure 20. Water desorption isotherms of moist soils  
and clay minerals



to the S-shaped curves reported by other investigators (4, 66, 67, 68, 78, 79, 80) who generally used the method of equilibrating the soil and clay mineral samples in desiccators which contained solutions of known vapor pressures.

It is evident from Figure 20 that the materials differ in their water adsorption behavior. The bentonite has the largest water adsorption capacity. This is due to its small particle size and a large internal surface area that is accessible for the adsorption of polar molecules like water. Edina and Fayette subsoils which contain montmorillonitic type clay mineral showed lower adsorption values, probably because of the smaller amount of clay size fraction in 100 g. of material. Illite and kaolinite were about the same in particle size distribution (Table 6), but the illite adsorbed more water. This difference is probably due to accessibility of some internal surface area in illite. In kaolinite only the external adsorption sites are available.

#### Interpretation of the $O_2$ Sorption Behavior of Moist Soils and Clay Minerals

The same general relationship between  $O_2$  sorption and moisture content was observed with several moist subsoil and clay mineral samples. In each case the amount of  $O_2$  sorbed decreased as the moisture decreased from an initially high moisture level. Then as the material became drier, the

the  $O_2$  sorption increased. At the higher moisture levels except for bentonite this relationship has been shown to arise simply from Henry's law for the solution of  $O_2$  in pure water. This interpretation of the observed changes in  $O_2$  sorption has been carried further by determining how the increase in sorption at the lower moisture levels is related to conditions that are known to affect the solubility of  $O_2$  in water. Salting-out and capillary effects are two of the factors that may cause the solubility of  $O_2$  in water in moist soil and clay mineral systems to differ from that expressed by Henry's law. In addition, the total amount of  $O_2$  sorbed may be affected by the occurrence of adsorption.

The water in partially dried soil and clay mineral systems is located in capillaries. Under this condition the water is under tension and the solubility of  $O_2$  in the water is affected because it is known that the solubility of a gas in water is influenced by the pressure on the water. An expression to calculate this capillary effect can be derived by considering the equilibrium condition in a system where  $O_2$  gas is in contact with water. The  $O_2$  will dissolve in the water until an equilibrium condition exists between the  $O_2$  in the gas and the liquid phases. At equilibrium,

$$\mu_{O_2,G} = \mu_{O_2,L} , \quad 1$$

where  $\mu_{O_2}$  is the chemical potential, G is the gas phase and L is the liquid phase.

By definition (61, p. 139)

$$\mu_{O_2} = \mu_{O_2}^{\circ} + RT \ln a_{O_2}, \quad 2$$

where  $\mu_{O_2}^{\circ}$  is the standard state chemical potential of  $O_2$ , and  $a_{O_2}$  is the activity of  $O_2$ . Then, assuming the standard state pressure to be  $P'$  for both gas and liquid phases, the condition for equilibrium may be written as

$$\mu_{O_2,G}^{\circ}(P') + RT \ln a_{O_2,G} = \mu_{O_2,L}^{\circ}(P') + RT \ln a_{O_2,L}. \quad 3$$

Since the chemical potential is related to the pressure  $P$  by the expression

$$\frac{\partial \mu}{\partial P} = \bar{V}, \quad 4$$

where  $\bar{V}$  is the partial molar volume, the standard state chemical potential of  $O_2$  in the liquid phase at pressure  $P''$  will be given by the expression

$$\mu_{O_2,L}^{\circ}(P'') = \mu_{O_2,L}^{\circ}(P') + \int_{P'}^{P''} \bar{V}_{O_2}^{\circ} dP. \quad 5$$

Assuming that  $\bar{V}_{O_2}^O$  remains constant, then

$$\mu_{O_2, L}^O(P'') = \mu_{O_2, L}^O(P') + \bar{V}_{O_2}^O [P'' - P'] . \quad 6$$

The equilibrium condition for the distribution of  $O_2$  in the gas phase at pressure  $P'$  and the liquid phase at pressure  $P''$  becomes

$$\begin{aligned} \mu_{O_2, G}^O(P') + RT \ln a_{O_2, G} = \\ \mu_{O_2, L}^O(P') + \bar{V}_{O_2}^O [P'' - P'] + RT \ln a_{O_2, L} . \end{aligned} \quad 7$$

Assuming ideal conditions

$$a_{O_2, G} = P_{O_2} \quad \text{and} \quad a_{O_2, L} = X_{O_2} , \quad 8$$

where  $P_{O_2}$  is the partial pressure of the  $O_2$  in the gas phase and  $X_{O_2}$  is the mole fraction of  $O_2$  in the liquid phase. Then from equations 7 and 8 the following general expression for the distribution of  $O_2$  may be obtained.

$$\frac{X_{O_2}}{P_{O_2}} = e^{\frac{-[\mu_{O_2, L}^O(P') - \mu_{O_2, G}^O(P')] - \bar{V}_{O_2}^O [P'' - P']}{RT}} . \quad 9$$

In the simplest case where the  $O_2$  is distributed between gas and liquid phases at the same temperature and pressure, that is,  $P'' = P'$ , equation 9 reduces to

$$\frac{x_{O_2}}{P_{O_2}} = e^{\frac{-[\mu_{O_2,L}^0(P') - \mu_{O_2,G}^0(P')]}{RT}} = \frac{1}{k}, \quad 10$$

where  $k$  is a constant. Equation 10 is simply Henry's law for the solubility of  $O_2$  in water.

In the special case where the liquid phase is in a capillary, the pressure in the liquid is due to the pressure of the gas phase  $P'$  and the pressure (tension) from capillary forces  $P$ , that is,  $P'' = P' + P$ . Then from equation 9

$$\frac{x_{O_2}}{P_{O_2}} = e^{\frac{-[\mu_{O_2,L}^0(P') - \mu_{O_2,G}^0(P')] - \bar{V}_{O_2}^0 P}{RT}} \quad 11$$

The pressure in water in a capillary arising from capillary forces (pressure in water under a concave surface) is given by the expression

$$P = - \frac{2\gamma_{H_2O}}{r}, \quad 12$$

where  $\gamma_{H_2O}$  is the surface tension of water and  $r$  is the radius of the capillary (61, p. 485).

Equation 11 and 12 may be combined and rearranged to give

$$\frac{x_{O_2}}{P_{O_2}} = e^{\frac{-[\mu_{O_2,L}^o(P') - \mu_{O_2,G}^o(P')]}{RT}} \cdot e^{\frac{2\gamma_{H_2O}\bar{V}_{O_2}}{rRT}} \quad 13$$

The decrease in vapor pressure of water in a capillary due to capillary forces is given by Kelvin's equation (61, p. 489)

$$\frac{P_{H_2O}^o}{P_{H_2O}} = e^{\frac{2\gamma_{H_2O}\bar{V}_{H_2O}}{rRT}}, \quad 14$$

where  $\gamma_{H_2O}$  = surface tension of water  
 $\bar{V}_{H_2O}$  = partial molar volume of water  
 $R$  = gas constant  
 $T$  = absolute temperature  
 $r$  = radius of the capillary  
 $P_{H_2O}^o$  = saturated vapor pressure of water  
 $P_{H_2O}$  = vapor pressure of water in the capillary.

Equation 14 can be rewritten in the form



$$\frac{2Y_{H_2O}}{e^{rRT}} = \left( \frac{P_{H_2O}^O}{P_{H_2O}} \right) \left( \frac{1}{\bar{V}_{H_2O}^O} \right) \quad 15$$

and combined with equation 13 to give the expression

$$\frac{x_{O_2}}{P_{O_2}} = e^{\frac{-[\mu_{O_2,L(P')} - \mu_{O_2,G(P')}]}{RT}} \cdot \left( \frac{P_{H_2O}^O}{P_{H_2O}} \right) \left( \frac{\bar{V}_{O_2}^O}{\bar{V}_{H_2O}^O} \right) \quad 16$$

This expression may be simplified on the basis of equation 10 to

$$\frac{x_{O_2}}{P_{O_2}} = \frac{1}{k} \cdot \left( \frac{P_{H_2O}^O}{P_{H_2O}} \right) \left( \frac{\bar{V}_{O_2}^O}{\bar{V}_{H_2O}^O} \right) \quad 17$$

By means of equation 17 the solubility of  $O_2$  in water held in a capillary under tension can be calculated if the vapor pressure of the water is known. Since  $P_{H_2O}^O$  is greater than  $P_{H_2O}$  when the water is in a capillary, the solubility of the gas in the water in partially dried soil and clay mineral systems should be greater than that of the non-capillary water.

To express the solubility of  $O_2$  in terms of cc. of  $O_2$  per g. of water instead of mole fraction, equation 17 may be altered to

$$\frac{V_{O_2}}{w} = K P_{O_2} \left( \frac{P_{H_2O}^O}{P_{H_2O}} \right) \left( \frac{\bar{V}_{O_2}^O}{\bar{V}_{H_2O}} \right), \quad 18$$

where  $K = \frac{55.5 \times 22.4}{k}$ ,  $V_{O_2}$  is the volume of  $O_2$  in cc. and  $w$  is the weight of water in grams.

As stated earlier, salts and other dissolved materials reduce the solubility of gases by binding some of the water and leaving less water to dissolve the gas. This effect can be combined with the capillary effect into a single equation. If  $w_T$  is the total weight of water present and  $w_H$  is the weight of water bonded by the soil surface and electrolytes, the water available to dissolve the  $O_2$  will be equal to  $(w_T - w_H)$ . Substituting this for  $w$ , equation 18 becomes

$$V_{O_2} = K P_{O_2} (w_T - w_H) \left( \frac{P_{H_2O}^O}{P_{H_2O}} \right) \left( \frac{\bar{V}_{O_2}^O}{\bar{V}_{H_2O}} \right) \quad 19$$

Equation 19 is the general expression by which the solubility of  $O_2$  in water (cc. per g. of water) may be cal-

culated when salting-out and capillary effects are present. If the salting-out effects are absent  $w_H = 0$ , and if capillary effects are absent  $P_{H_2O}^O = P_{H_2O}$  and the equation is then simply that for Henry's law with the solubility expressed as cc. per g. of water instead of mole fraction.

The amount of  $O_2$  that would dissolve in the water of the moist Edina and Fayette subsoil samples was calculated by means of Equation 19. The water vapor pressure values reported in the previous section for these moist samples were used to calculate  $P_{H_2O}^O/P_{H_2O}$ .  $\bar{V}_{O_2}$  and  $\bar{V}_{H_2O}$  were calculated using the density of liquid  $O_2$  of 1.14 g./cc. (43, p. 434) and that of  $H_2O$  of 1.00 g./cc. (43, p. 1788).

The amount of water unavailable to dissolve  $O_2$  ( $w_H$ ) was not known. It was therefore assumed for these calculations that  $w_H = 0$ . A comparison of the  $O_2$  solubility values for the Fayette and Edina subsoils calculated at different moisture levels and the experimentally determined  $O_2$  sorption curves is shown in Figures 21 and 22, respectively.

At the higher moisture levels  $P_{H_2O} = P_{H_2O}^O$  so the calculated values are simply those predicted by Henry's law and as shown previously these calculated solubility values and the experimental sorption values are about the same. At lower moisture levels where  $P_{H_2O} < P_{H_2O}^O$ , the calculated values also fit the experimental data very well. Since  $w_H$  was assumed to be zero in these calculations, there must have been little salting-out effect in this moisture range. Instead,

Figure 21. Comparison of experimental and calculated  $O_2$  sorption values for moist Fayette subsoil

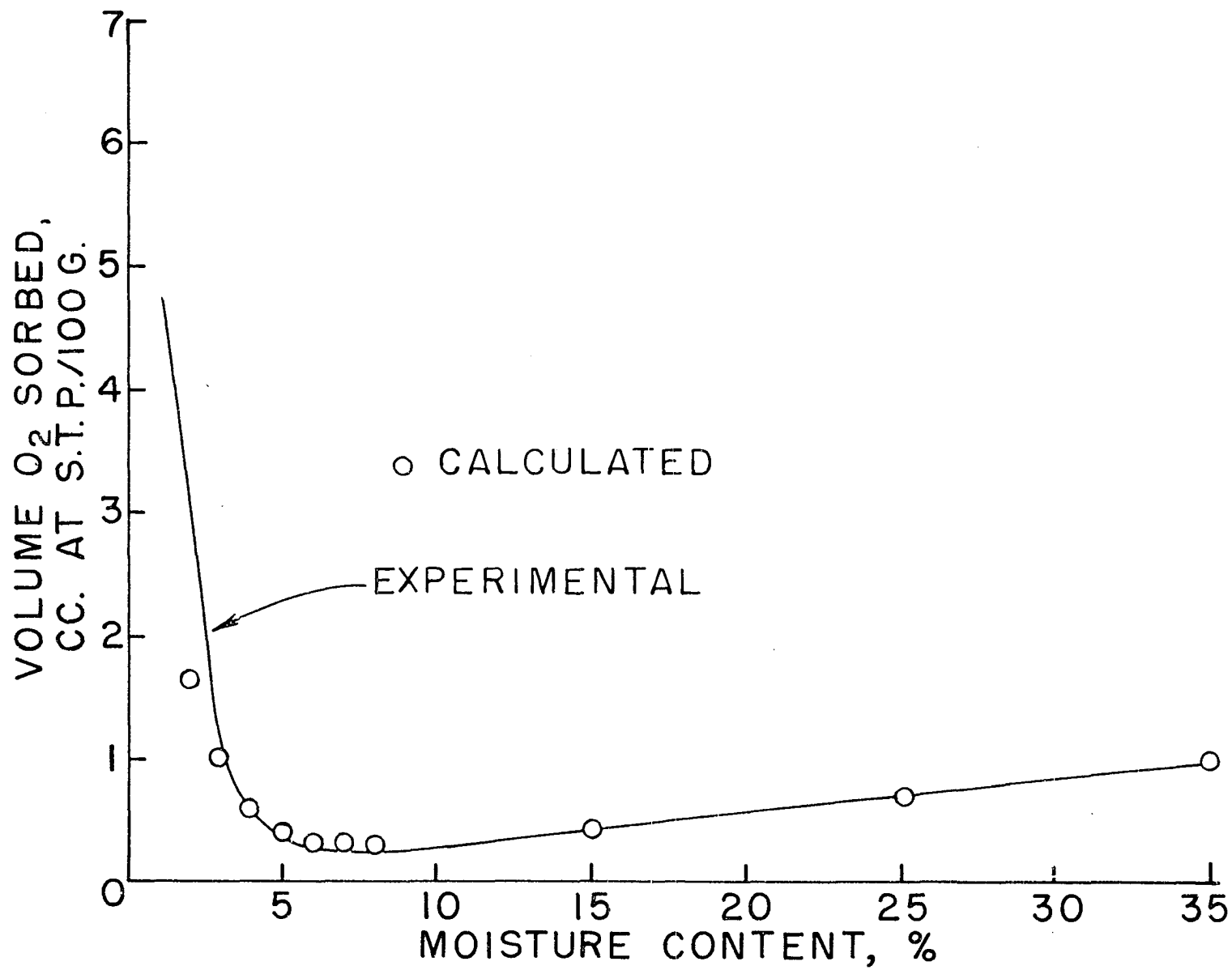
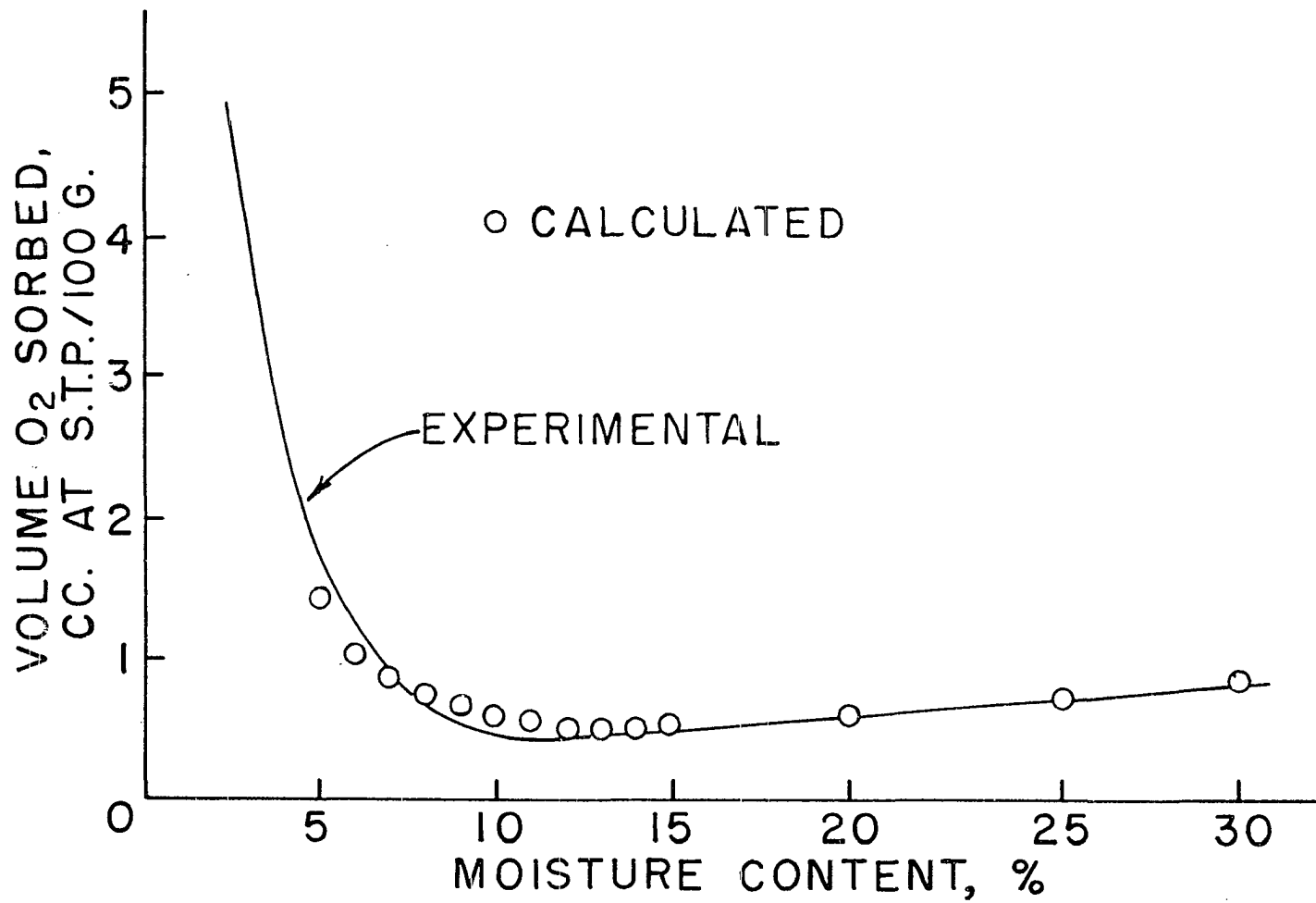


Figure 22. Comparison of experimental and calculated  $O_2$  sorption values for moist Edina subsoil sample 2



the vapor pressure change and  $O_2$  sorption change that occurred when the moisture content was decreased must have been mainly due to capillary effects.

The gas sorption values for the drier materials were largely determined by the process of adsorption rather than absorption. Thus, the solubility values calculated with equation 19 were lower than the experimental sorption values in the very dry materials. Also, because of the large increase in adsorption that occurred on drying the soils it is impossible to say if salting-out effects occurred at the very low moisture levels. In any event, the salting-out effect would have to be small because the solubility values are already small in this moisture range.



## OVEN-DRIED SOILS AND CLAY MINERALS

## Gas Sorption by Oven-Dried Soils and Clay Minerals

It was observed in the  $O_2$  and  $CO_2$  measurements with moist soils and clay minerals that the soils adsorbed more gas than bentonite when the materials were dried at  $110^\circ C$ . To examine this behavior further, the adsorption of these gases by other soils and clay minerals was determined and the effect of various treatments on their adsorptive capacity was studied. The effect of oven drying the samples at various temperatures was one of these treatments.

The soil samples were air-dried and passed through a 0.5 mm. sieve. The clay minerals bentonite, illite and kaolinite were already in a finely divided state and were used without further treatment. Vermiculite was also used without grinding or sieving even though the particles were large. The air-dried samples were dried for 48 hours at  $110^\circ C$ . in a drying oven, and then at  $250^\circ$ ,  $500^\circ$ , and  $750^\circ C$ . in a muffle furnace. Porcelain dishes were used when the samples were heated at the higher temperatures. After each period of drying, the samples were placed in the sorption flask of the apparatus and adsorption isotherms at  $25^\circ C$ . were obtained first for  $O_2$  and then  $CO_2$  using the constant volume method described in the section on methods.

Similar adsorption isotherms were obtained with the various oven-dried materials. Therefore, only the isotherms of  $O_2$  and  $CO_2$  for the oven-dried Edina subsoil are presented in Figures 23 and 24, respectively, to show the type of curves obtained. The volume of gas, corrected to S. T. P., adsorbed per 100 g. of material, has been plotted against the partial pressure of the gas.

The  $O_2$  adsorption isotherms obtained for the Edina subsoil sample that was heated at  $110^\circ$ ,  $250^\circ$ ,  $500^\circ$ , and  $750^\circ$  C. were all linear. The  $CO_2$  isotherms, on the other hand, were curvilinear, but at the low adsorption levels ( $750^\circ$  C. treatment) the curvature was quite small. Alten and Loofmann(5), Jamison (44), and Wiesmann and Neumann (88) reported linear air adsorption isotherms between  $20^\circ$  and  $25^\circ$  C. with different soils and clay minerals. Emmett et al. (20) and Makower et al. (57) observed linear  $O_2$  and curvilinear  $CO_2$  adsorption isotherms for several soils. Kuron (49), and Wieden and Baldwin (87) also obtained curvilinear  $CO_2$  adsorption isotherms for their soil and clay samples at  $20^\circ$  C. The curves obtained in this study were thus comparable to those obtained by other investigators at the same temperature. It may be noted that the previous heating temperature did not affect the shape of the curve even though the adsorption capacity of the material was decreased.

Figure 23. Oxygen adsorption isotherms for Edina subsoil sample 2 after heat treatment at 110°, 250°, 500° and 750° C.

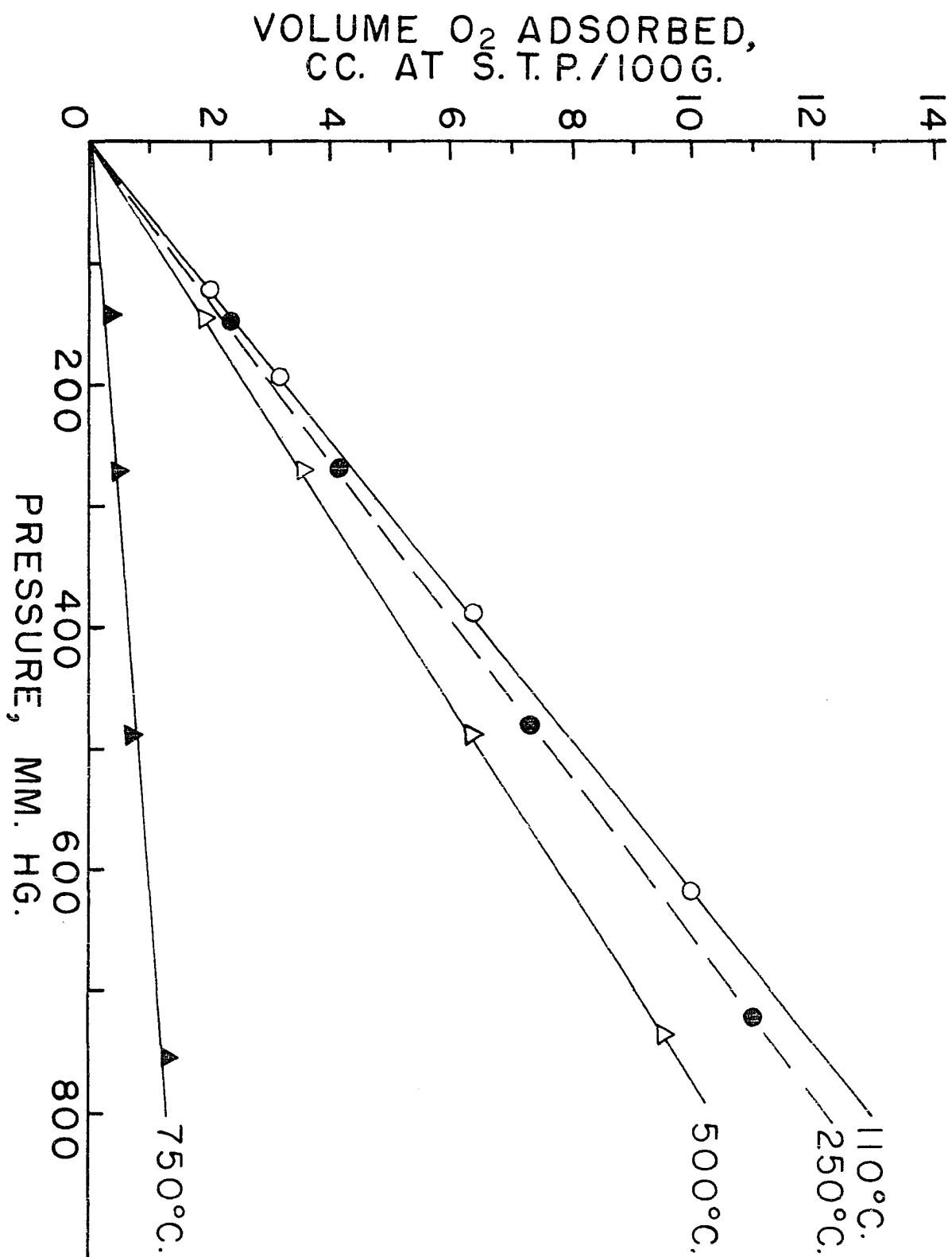
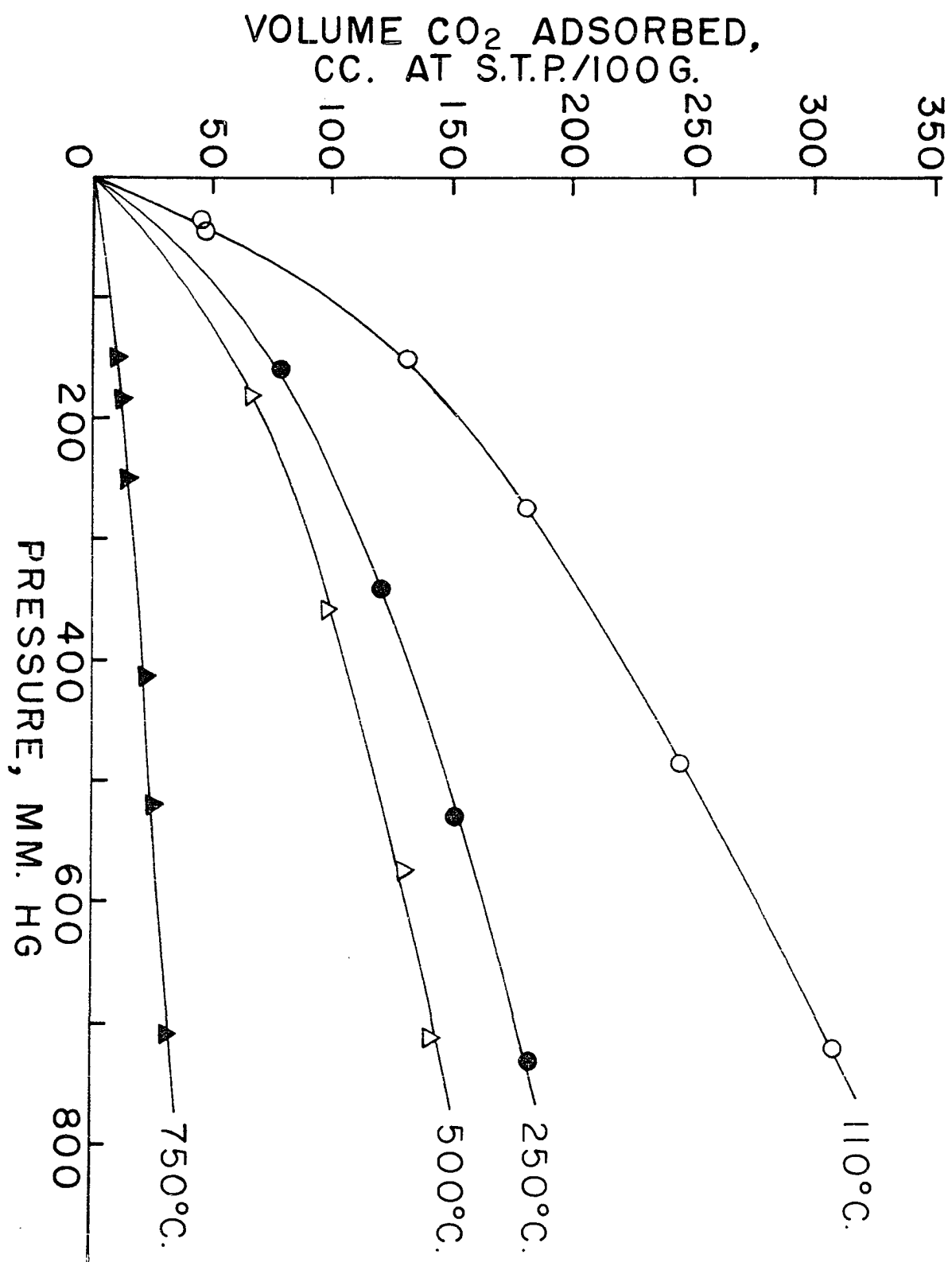


Figure 24. Carbon dioxide adsorption isotherms for Edina subsoil sample 2 after heat treatment at 110°, 250°, 500° and 750° C.



It has been stated that gases with higher critical temperatures are generally adsorbed to a greater extent by a solid than those with lower values (14, p. 12). Thus, it is not surprising that the relative adsorbability is  $H_2O > CO_2 > O_2$  since the critical temperatures are  $374.0^\circ$ ,  $31.1^\circ$  and  $-118.8^\circ$  C., respectively (43, p. 1907).

The difference in the shape of the  $H_2O$ ,  $CO_2$  and  $O_2$  adsorption isotherms does not mean that different adsorption processes are involved. Both linear and curvilinear types of adsorption isotherms can exist for the same gas on the same material according to Brunauer (14, p. 14). He has given examples where the isotherm was linear at a high adsorption temperature and curvilinear at a lower adsorption temperature. The difference in the shape of the isotherms obtained in this study (S-shaped water vapor curves, curvilinear  $CO_2$  curves and linear  $O_2$  curves) occurred because the experimental temperature of  $25^\circ$  C. was high relative to the critical temperature of  $O_2$ , about equal to that of  $CO_2$  and lower than that of  $H_2O$ .

The volumes of  $O_2$  and  $CO_2$  adsorbed by various soils and clay minerals at  $25^\circ$  C. and a partial pressure of 760 mm. of Hg are given in Table 5. These values were taken from adsorption isotherms that were determined for these materials after the various heat treatments.

Table 5. Volume of gas adsorbed at 25° C. and 760 mm. of Hg pressure by soils and clay minerals, cc. at S.T.P./100 g., after they were oven-dried at different temperatures

| Soil             | Oven-dried temperature, ° C. |                    |                   |                 |                   |                 |                |                 |
|------------------|------------------------------|--------------------|-------------------|-----------------|-------------------|-----------------|----------------|-----------------|
|                  | 110°                         |                    | 250°              |                 | 500°              |                 | 750°           |                 |
|                  | O <sub>2</sub>               | CO <sub>2</sub>    | O <sub>2</sub>    | CO <sub>2</sub> | O <sub>2</sub>    | CO <sub>2</sub> | O <sub>2</sub> | CO <sub>2</sub> |
| Clarion, subsoil | 6.70                         | 142.0              | 5.08              | 91.0            | 4.43              | 77.0            | 0.82           | 13.5            |
| Clarion, surface | 6.54                         | 149.5              | ----              | ----            | ----              | ----            | ----           | ----            |
| Edina, subsoil   | 12.25                        | 322.0              | 11.60             | 186.0           | 9.85              | 150.0           | 1.25           | 33.6            |
| Edina, surface   | 6.30                         | 150.0              | 5.57              | 110.0           | 4.30              | 79.0            | 1.10           | 16.4            |
| Ida, "           | 6.80                         | 186.0              | ----              | ----            | ----              | ----            | ----           | ----            |
| Lagonda, "       | 7.33                         | 168.0              | ----              | ----            | ----              | ----            | ----           | ----            |
| Luton, "         | 12.50                        | 316.0              | 11.1              | 191.0           | 10.80             | 203.0           | ----           | ----            |
| Webster, "       | 9.50 <sup>a</sup>            | 248.0 <sup>a</sup> | 8.62              | 156.0           | 6.20              | 108.0           | 0              | 5.77            |
| Zwingle, subsoil | 13.40                        | 377.0              | 11.45             | 215.0           | 11.20             | 159.0           | 1.72           | 27.8            |
| Bentonite        | 6.50 <sup>a</sup>            | 141.0              | 5.58              | 113.0           | 6.06 <sup>a</sup> | 114.0           | 0              | 7.50            |
| Illite           | 9.90 <sup>a</sup>            | 206.0              | 9.35 <sup>a</sup> | 173.0           | 5.28              | 116.0           | .65            | 24.8            |
| Kaolinite        | 2.32 <sup>b</sup>            | 41.5               | 2.30              | 39.5            | 1.90              | 21.0            | 1.77           | 15.2            |
| Vermiculite      | 2.60                         | 22.0               | 2.20              | ----            | 2.25              | ----            | 0              | 12.0            |

<sup>a</sup>Mean of duplicate determinations

<sup>b</sup>Mean of triplicate determinations



Vermiculite has an expanding type lattice but it adsorbed small amounts of  $O_2$  and  $CO_2$  like kaolinite which has a non-expanding type lattice. This would indicate that only a small part of the internal surface of the dry vermiculite was accessible to the gases. The vermiculite particles were much larger in size than the kaolinite since it was a commercial exfoliated material. Thus, to adsorb as much gas as the kaolinite which was mainly  $<20\mu$  in size, some gas adsorption must have occurred on internal surfaces of the vermiculite sample. None of the soils adsorbed as little gas as these two clay minerals.

The Zwingle and Edina subsoils, and the Luton and Webster surface soils adsorbed much more  $CO_2$  and  $O_2$  than bentonite at the  $110^\circ$ ,  $250^\circ$  and  $500^\circ$  C. heat treatments. Thus, it is evident that soils other than the Edina subsoil are also capable of adsorbing more of these gases than bentonite.

Makower et al. (57), and Nelson and Hendricks (65) have also observed that soils may adsorb more gas than bentonite. The latter authors postulated that the low adsorption by bentonite is due to the contraction of the lattice. It was observed in Figure 8 that the amount of  $O_2$  sorbed increased and then decreased when the moist bentonite was dried to a  $110^\circ$  C. oven-dry state. Brooks (13) obtained the same results with  $N_2$  and he concluded that the gas was adsorbed be-

tween the plates when water was first removed, but as more water was removed the lattice contracted and the internal surface of the clay mineral became inaccessible for gas adsorption.

Call (16) found that Ca montmorillonite adsorbed more ethylene dibromide after it was treated to approximately 3, 6 and 8% moisture than at 0% moisture. He attributed this increase in adsorption to an expansion of the lattice which allowed the gas to enter between the plates to the interlamellar adsorption sites.

In contrast with bentonite, the Edina (Figure 4) and the Fayette (Figure 5) moist subsoil samples showed a continuous increase in gas adsorption as they were dried to a 110° C. oven-dry state. Since much of the clay in these soil samples is an expanding lattice montmorillonite type mineral, this difference in behavior on drying and the greater gas adsorption by the oven-dried soils can only be explained on the basis that something keeps the soil clay lattice from contracting when the materials were dried.

Some of the data from Table 5 have been plotted in Figures 25 and 26 to compare the materials in regard to the effect of the heat treatments. The adsorptive capacity of the soils decreased when the heating temperature was increased. The bentonite, kaolinite and vermiculite samples, on the other hand,

Figure 25. Volume of  $O_2$  adsorbed at  $25^\circ$  C. and 760 mm. of Hg pressure by soils and clay mineral samples after they were heated at  $110^\circ$ ,  $250^\circ$ ,  $500^\circ$  and  $750^\circ$  C.

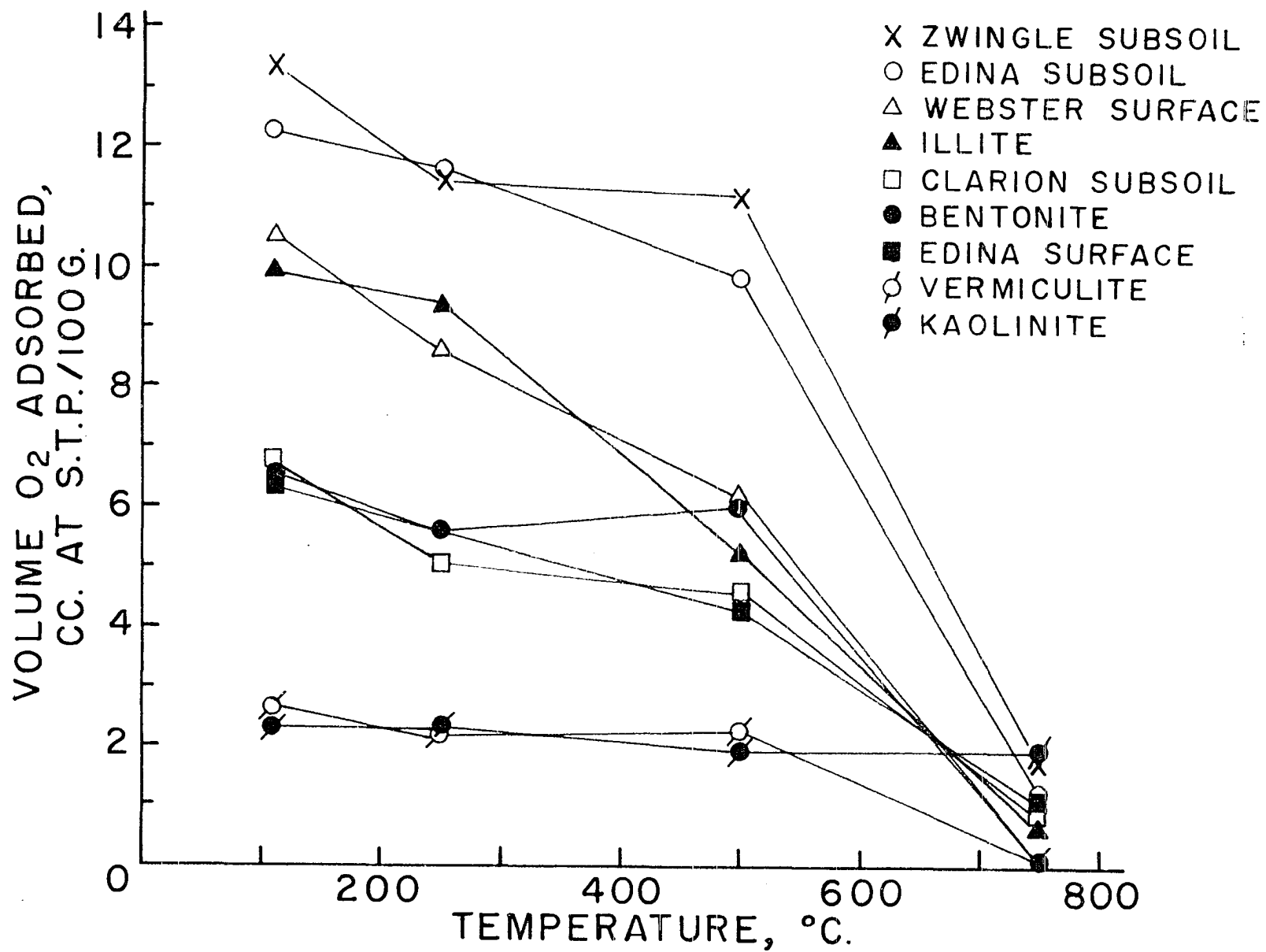
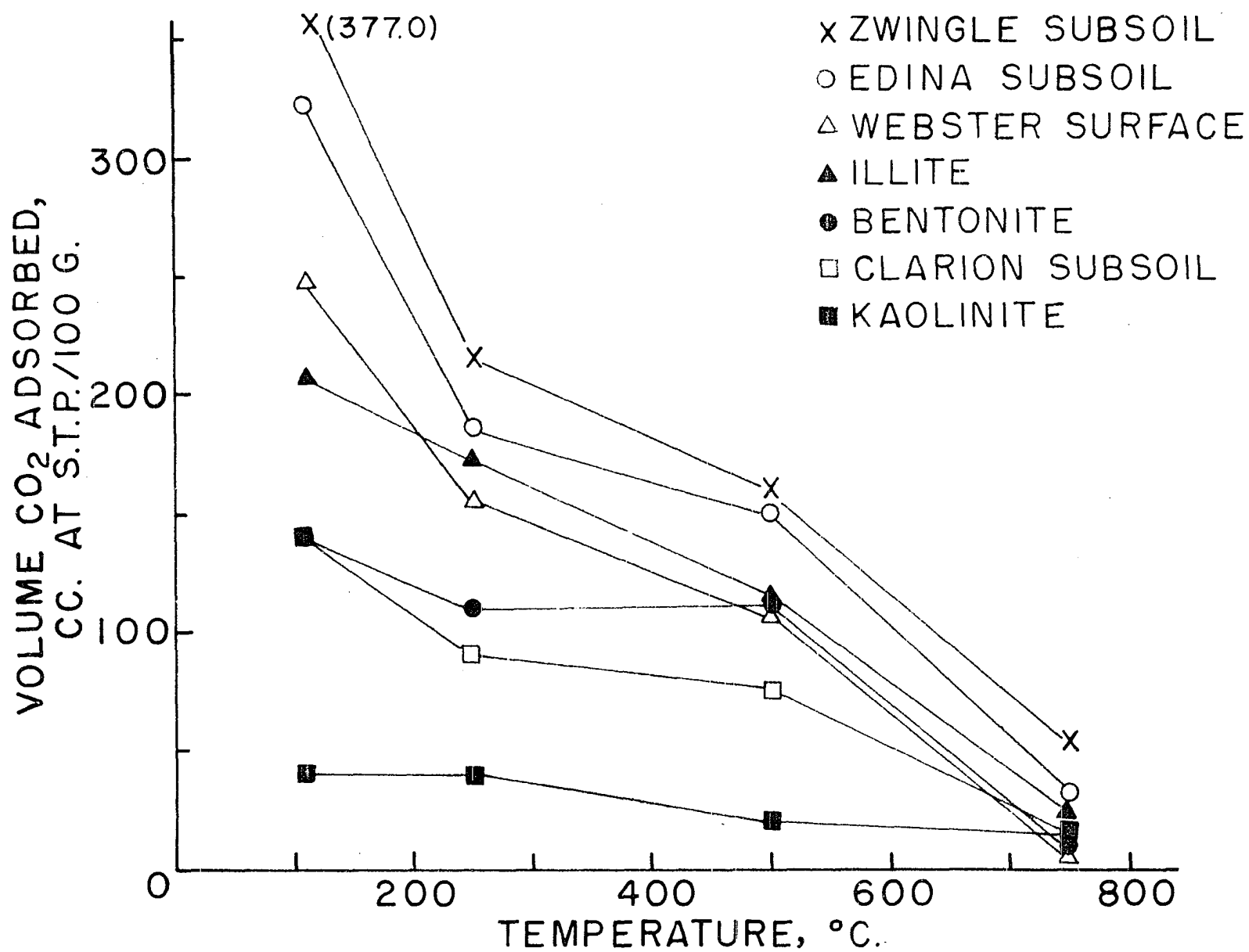


Figure 26. Volume of CO<sub>2</sub> adsorbed at 25° C. and 760 mm. of Hg pressure by soil and clay mineral samples after they were heated at 110°, 250°, 500° and 750° C.



were not greatly affected by temperatures up to  $500^{\circ}$  C. Apparently, there was a small effect of temperature on the soil property that caused soils to adsorb more gas than bentonite. The soils continued to adsorb more gas than bentonite, however, even after they were heated at  $500^{\circ}$  C. The  $750^{\circ}$  C. heat treatment decreased the adsorptive capacity of the soils and the clay minerals because the materials were sintered.

The amounts of  $O_2$  and  $CO_2$  adsorbed by the soils and clay minerals after heat treatments of  $110^{\circ}$ ,  $250^{\circ}$  and  $500^{\circ}$  C. are compared in Figure 27. There was a linear relationship between the amount of  $O_2$  and the amount of  $CO_2$  adsorbed by these materials after each heat treatment. The temperature of heating, however, had a differential effect on the adsorption of the two gases. When the heating temperature was increased from  $110^{\circ}$  to  $250^{\circ}$  C. the adsorption of both gases was decreased, but the  $CO_2$  adsorption was decreased more than the  $O_2$ . This difference was particularly large in the case of the soil samples that adsorbed large amounts of gas. Thus, the slope of the curves relating  $O_2$  and  $CO_2$  adsorption changed when the heating temperature was increased from  $110^{\circ}$  to  $250^{\circ}$  C. Heating to  $500^{\circ}$  C. produced little additional differential effect.

A comparison of the amounts of  $O_2$  and  $H_2O$  adsorbed by some of the  $110^{\circ}$  C. oven-dried materials is shown in Figure 28.

Figure 27. Relationship between the  $O_2$  and  $CO_2$  adsorbed by soil and clay mineral samples that were heated at  $110^\circ$ ,  $250^\circ$  and  $500^\circ$  C.



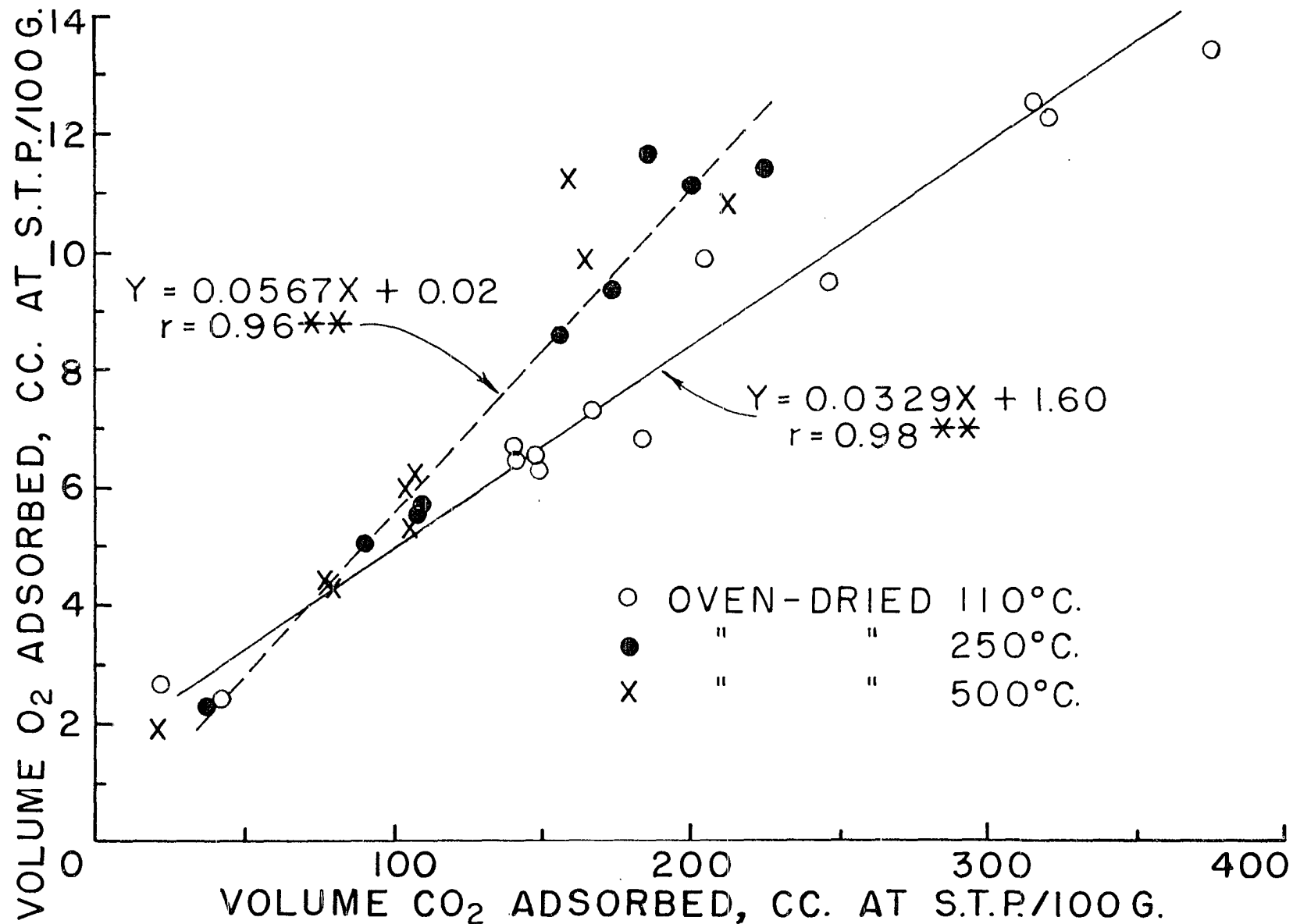
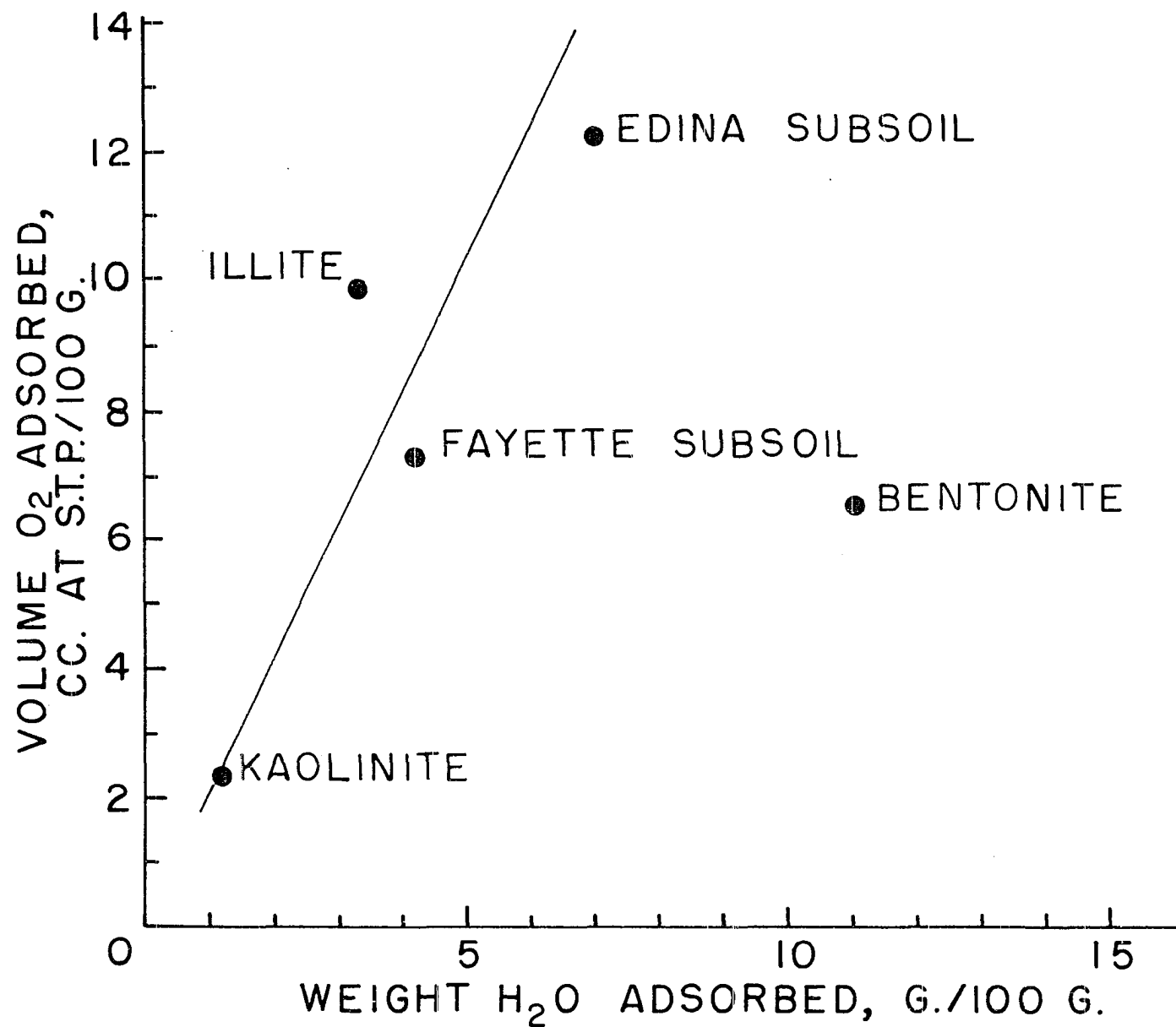


Figure 28. Relationship between the adsorption of  $O_2$  and  $H_2O$  by soil and clay mineral samples. (Bentonite point omitted when curve drawn)



The  $\text{H}_2\text{O}$  adsorption values were obtained from the vapor pressure-moisture content curves (Figure 20) at a vapor pressure of 10 mm. of Hg. The  $\text{O}_2$  adsorption values were obtained at a pressure of 760 mm. of Hg. In the case of illite, kaolinite and the subsoil samples of Fayette and Edina there was a good relationship between the amount of  $\text{O}_2$  and  $\text{H}_2\text{O}$  adsorbed. Alten and Loofmann (5) has also observed a linear relationship between the amount of air adsorbed by the oven-dried soils and the amount of  $\text{H}_2\text{O}$  adsorbed on air-dried soils.

Bentonite did not behave like the soils, illite and kaolinite in that it adsorbed much more  $\text{H}_2\text{O}$  relative to  $\text{O}_2$ . It is known that the lattice of dry, expanding lattice clay minerals is expanded by the polar  $\text{H}_2\text{O}$  molecules which penetrate between the layers of the lattice. The internal surface of the bentonite was therefore accessible to  $\text{H}_2\text{O}$  even though it was not accessible to  $\text{O}_2$ . On the other hand, the  $\text{O}_2$ - $\text{H}_2\text{O}$  adsorption relationship for the Fayette and Edina subsoils was similar to that for the non-expanding illite and kaolinite minerals even though these soils contain expanding montmorillinite type clay minerals. That is, the same surface area was accessible to both  $\text{O}_2$  and  $\text{H}_2\text{O}$  in these materials. This evidence supports the idea that the lattice of these soil clay minerals did not contract completely on drying and that the internal surface of the dry materials was still accessible to  $\text{O}_2$  adsorption.

In the  $O_2$ - $CO_2$  comparison (Figure 27), bentonite behaved like the soils and non-expanding clay minerals. Apparently the  $CO_2$  molecules are not polar enough to penetrate between the layers of the contracted lattice of bentonite.

### Gas Adsorption and Clay Content

Another factor that is known to affect the adsorption capacity of any solid is its particle size distribution. Therefore, the particle size distribution of the materials was determined using the pipette method of analysis described by Kilmer and Alexander (47). The percentage of particles in each sample that was  $<20$ ,  $<2$ ,  $<1$ ,  $<0.5$  and  $<0.25\mu$  in size is presented in Table 6.

The relationship between the amount of  $<2\mu$  fraction and the volume of  $O_2$  adsorbed by the  $110^\circ C$ . heat-treated materials is shown graphically in Figure 29. A regression equation of  $Y = 0.187 X^{2.72}$  and a correlation coefficient of  $r = 0.93$  were obtained for the soils alone. The values for the clay minerals which were not included in the calculations are labeled individually. The relationship between the  $<2\mu$  fraction and the adsorptive capacity of the soils is good. Other investigators (11, 65, 76) using other adsorbates such as  $N_2$ , chloropicrin and ethylene glycol reported similar relationships and it is now generally accepted that the clay size fraction in the soil is the principle adsorbent. The

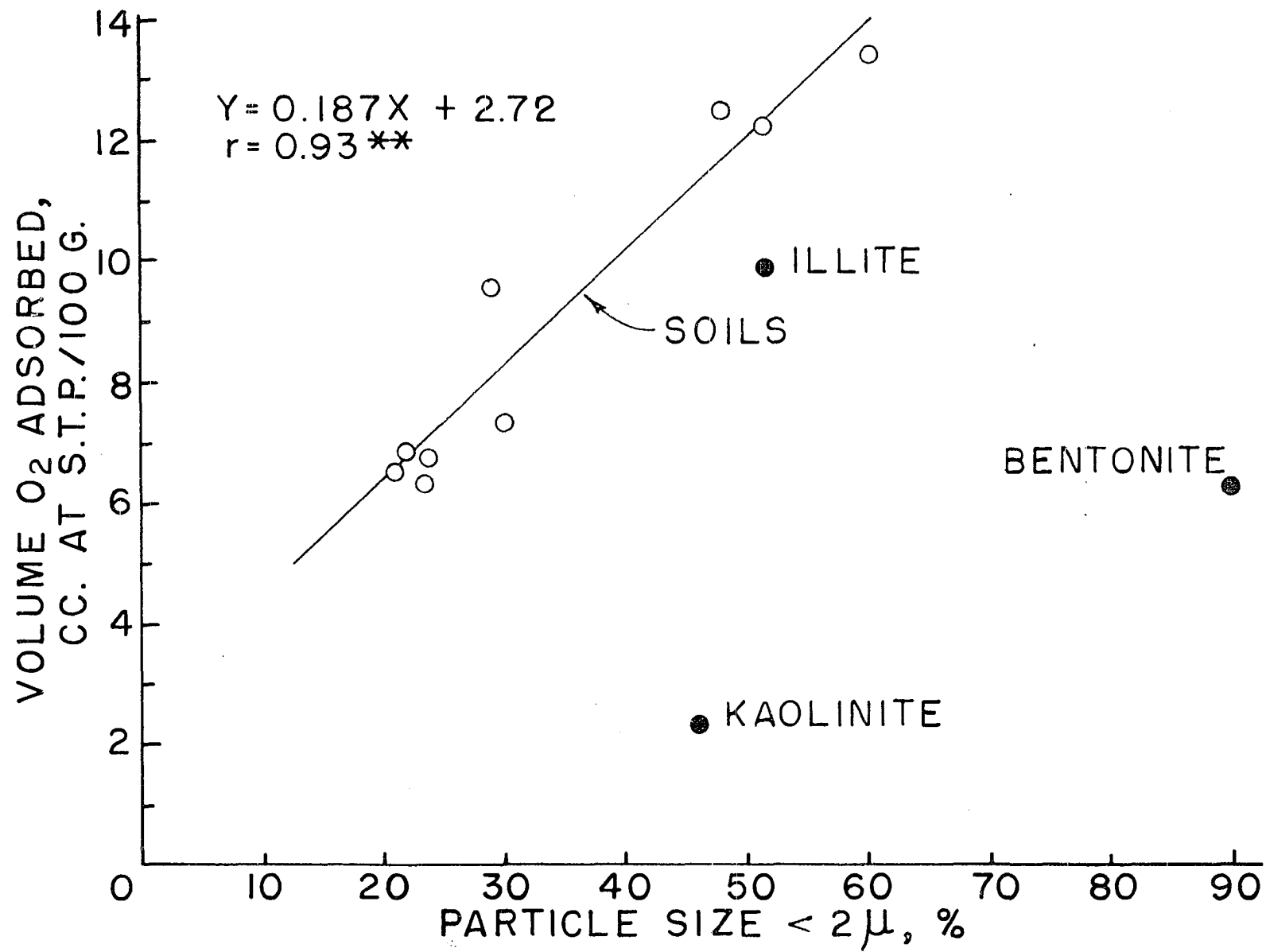
Table 6. Particle size distribution of soils and clay minerals

| Material         | Particle size, % |          |          |            |             |
|------------------|------------------|----------|----------|------------|-------------|
|                  | <20 $\mu$        | <2 $\mu$ | <1 $\mu$ | <0.5 $\mu$ | <0.25 $\mu$ |
| Clarion, subsoil | 40.21            | 23.64    | 20.11    | 18.31      | 16.16       |
| Clarion, surface | 38.90            | 21.42    | 19.15    | 17.71      | 14.54       |
| Ida, "           | 44.52            | 21.96    | 18.91    | 15.74      | 11.91       |
| Lagonda, "       | 61.52            | 30.04    | 27.17    | 24.95      | 21.12       |
| Luton, "         | 78.39            | 47.99    | 42.31    | 36.62      | 29.32       |
| Webster, "       | 56.73            | 29.20    | 27.53    | 24.71      | 20.52       |
| Bentonite        | 95.15            | 90.05    | 88.10    | 81.68      | 55.80       |
| Edina, subsoil   | 82.70            | 51.58    | 47.39    | 45.78      | 40.03       |
| Edina, surface   | 62.35            | 23.34    | 19.33    | 15.98      | 13.28       |
| Illite           | 91.38            | 51.58    | 35.78    | 23.22      | 14.54       |
| Kaolinite        | 93.23            | 46.02    | 32.61    | 24.00      | 14.42       |
| Zwingle          | 96.04            | 60.20    | 50.62    | 45.90      | 38.84       |

data here, however, indicate that the clay mineral samples do not show the same relationship between adsorption and clay content as the soils.

If adsorption was limited to the external surface of the particles, the <2 $\mu$  material would largely determine the surface available for gas adsorption and all materials should fit the same O<sub>2</sub> adsorption-clay content relationship. Devia-

Figure 29. Relationship between the amount of  $O_2$  sorbed and the  $<2\mu$  clay in various soils and clay mineral samples





tions from this must be due to adsorption by materials other than the clay in the sample, or differences in the availability of internal surfaces for adsorption. It will be shown in the next section that the organic matter did not contribute much to the adsorptive capacity of soils. Since this is the only other material that could contribute to the adsorptive power of soils, the difference in adsorptive capacity is more likely due to the accessibility of internal surfaces.

A comparison of kaolinite and bentonite based on an equivalent amount of  $<2\mu$  clay indicates that bentonite adsorbed only 40% more gas. Thus, most of the  $O_2$  adsorptive capacity of bentonite must be due to its external surfaces. The soils, on the other hand, all show higher adsorption than bentonite or kaolinite on the basis of equal amounts of clay size particles. Thus, much of their adsorption must be in the internal surface. It should be noted that the surface and subsoils all behave alike and that the difference in adsorptive capacities exhibited by the soils used is largely due to the amount of clay present. Thus, the Edina surface sample adsorbed about the same amount of gas as the bentonite, but on an equivalent clay basis it adsorbed much more, just as the Edina subsoil did.

Illite is normally considered to be primarily a non-expanding lattice mineral. The material investigated, however,

is Goose Lake Grundite and it contains inter-stratified expanding and non-expanding lattice minerals. Its higher adsorptive capacity in comparison to kaolinite would suggest that some adsorption occurs on internal surfaces. In this regard it is more like the soils than bentonite. It is also more like the soils than bentonite or kaolinite in that it contains organic matter. It is possible that the continued accessibility of the internal surface of dry soils and illite is due to this organic matter.

#### Gas Adsorption and Organic Matter

It is generally accepted that the inorganic silicate clay minerals are responsible for much of the gas adsorption in soils. Variable results have been reported, however, for the adsorption of gases by the organic constituents present. Jamison (44) found that an organic colloid separated from a sandy soil adsorbed little air. Stark (76) noted that the organic matter adsorbed relatively small amount of chloropicrin. Call (16), on the other hand, using ethylene dibromide observed a good correlation between sorptive capacity and organic matter content, but this may be due to the greater polar character of the ethylene dibromide. Further evidence that larger quantities of polar molecules can be held by the organic fraction is shown by the results of Feustel and Byers (25) which show that peat had a high moisture retaining capacity.

Mortland (62) reported that muck materials adsorbed a very large amount of  $\text{NH}_3$  in comparison to the silicate clays.

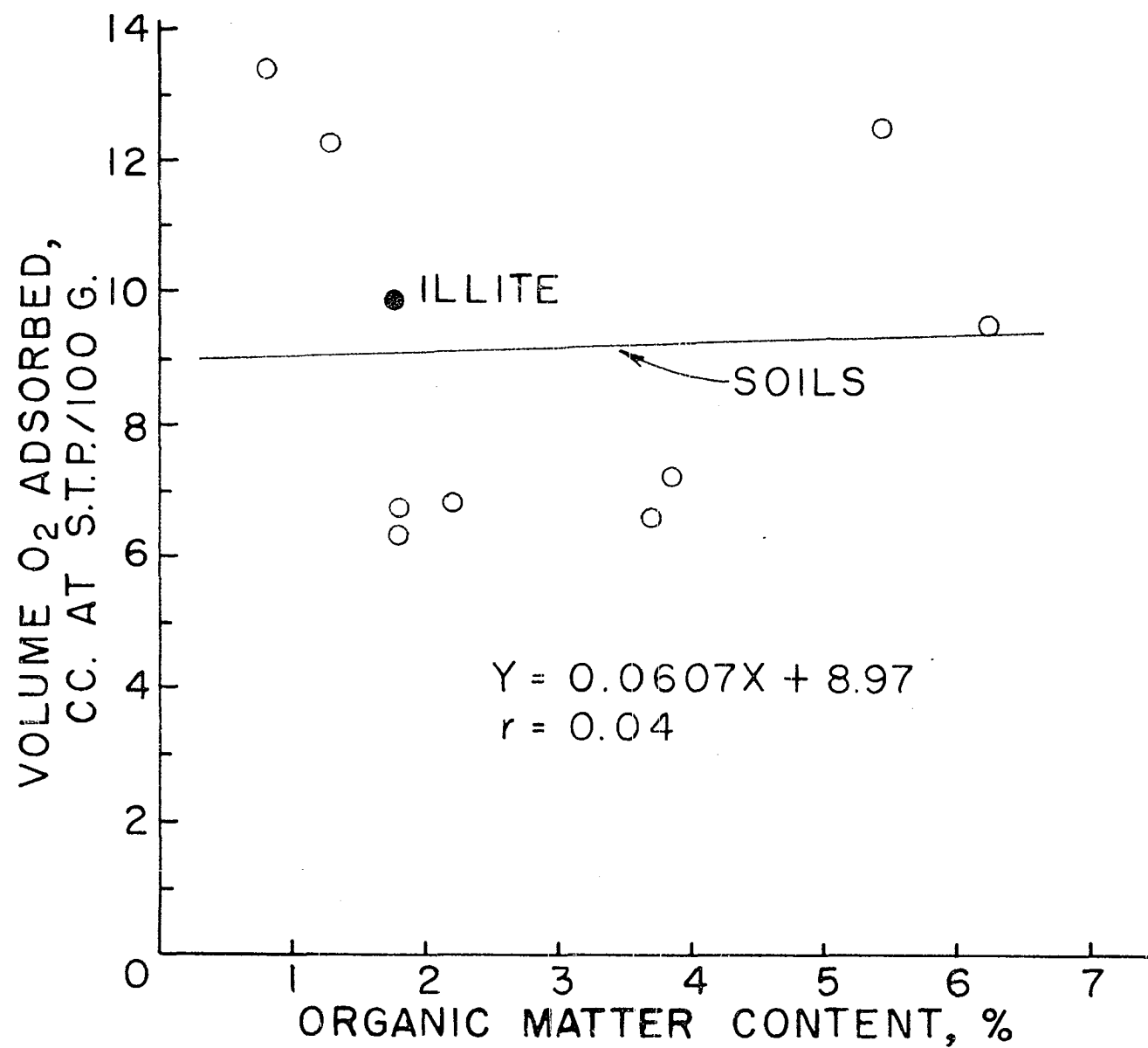
It was known that the soil and illite samples used in the present investigation contained more organic matter than bentonite or kaolinite. In addition, the results presented in the previous section indicated that there was a difference between these two groups of materials in regard to the amount of  $\text{O}_2$  adsorbed per g. of clay present. Attention was therefore directed toward a study of the effects of organic constituents on the adsorption of  $\text{O}_2$  by these samples.

#### Relation of $\text{O}_2$ adsorption to organic matter content

The effect of organic material on  $\text{O}_2$  adsorption was first evaluated by determining the organic matter in the materials and relating it to the amount of  $\text{O}_2$  adsorbed by the  $110^\circ \text{C}$ . oven-dried materials. Total C was determined by the dry combustion method described by Black (9, p. 12). This value was converted to organic matter by multiplying the total C by the factor 1.724 (84).

The organic matter content in the soils ranged from 0.8 to 6.25%. Illite contained 1.76% organic matter while the kaolinite and bentonite clay minerals were free of organic materials. The results of the organic matter determinations are plotted in Figure 30 with the  $\text{O}_2$  adsorptive capacities of the materials.

Figure 30. Relationship between the amount of  $O_2$  adsorbed and the organic matter content in soils and illite



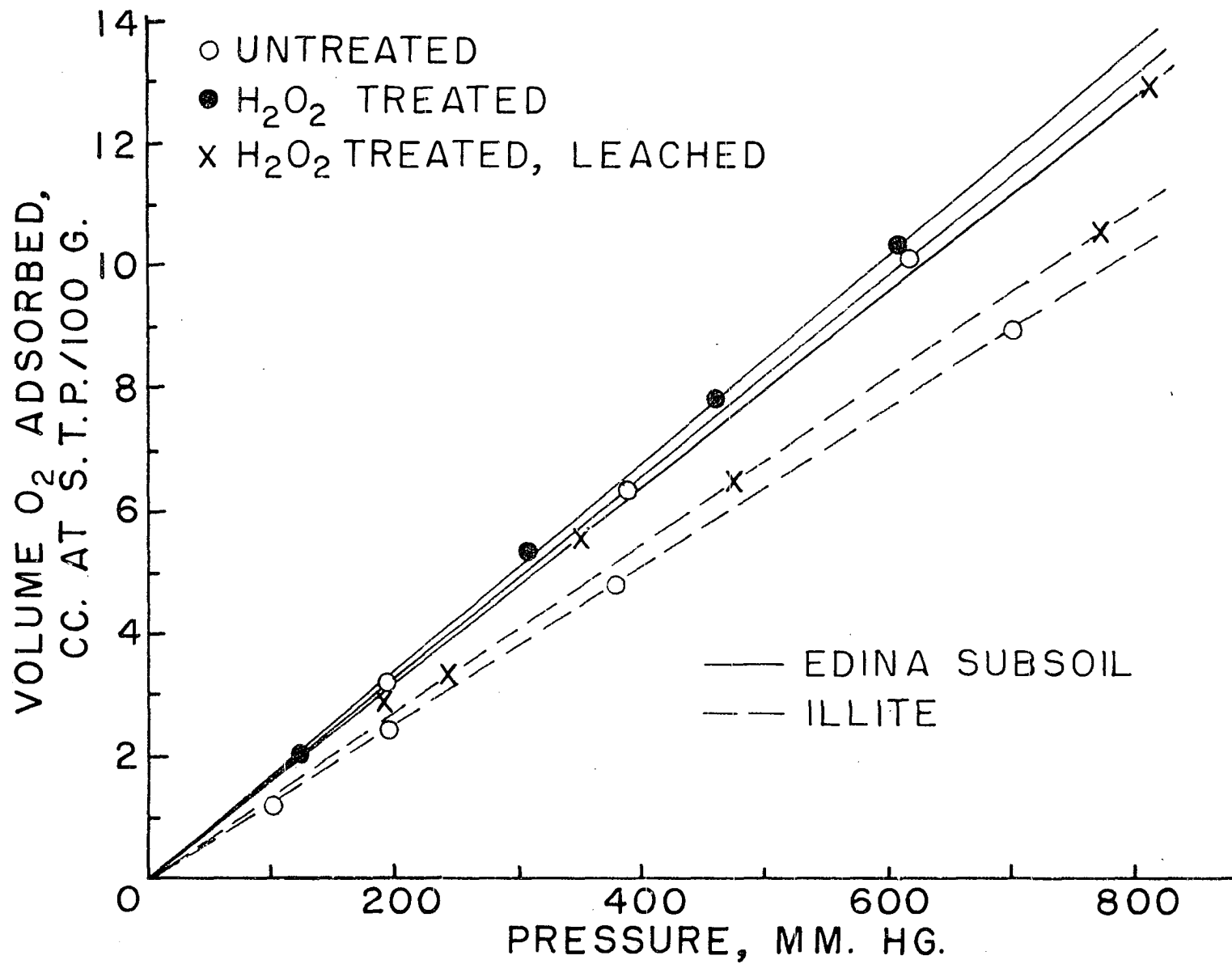
It is evident that there is essentially no relationship between the organic matter content and the amount of  $O_2$  adsorbed. This relationship is not improved when differences due to clay content are removed by plotting the organic matter content with the amount of  $O_2$  adsorbed per g. of clay in these materials.

#### Organic matter destruction

Although the relationship between  $O_2$  adsorption and organic matter content was poor, it was possible that the difference in  $O_2$  adsorption by the bentonite and the soils was due to an effect of part of the organic matter on adsorption. An attempt was made to remove this effect by oxidizing and removing as much of the organic matter as possible.

Edina subsoil and illite samples were treated with 30%  $H_2O_2$  to destroy the organic matter fraction. One sample of the peroxide treated Edina subsoil was used without being leached, but another Edina sample and the illite sample were leached with water after the peroxide treatments. The organic matter for the Edina subsoil was decreased from 1.3 to 0.6% in the peroxide treated unleached sample. The organic matter in the other samples was not determined. Oxygen adsorption isotherms were determined for the peroxide treated materials and compared with the adsorption isotherms of the untreated samples. The results obtained are shown in Figure 31.

Figure 31. Effect of  $\text{H}_2\text{O}_2$  treatment on the  $\text{O}_2$  adsorption isotherms of  $110^\circ \text{C}$ . oven-dried Edina subsoil sample 2 and illite





Neither the Edina subsoil nor the illite exhibited an appreciable change in adsorption of  $O_2$  when part of the organic matter was oxidized with  $H_2O_2$ . Apparently the peroxide treatment did not affect the adsorption sites nor their accessibility. In addition, that part of the organic material destroyed by the peroxide did not contribute very much to the adsorption of  $O_2$  by these materials.

#### Organic matter treatment

Numerous investigations have shown that polar organic molecules may occupy interlamellar positions in expanding lattice type clay minerals. Bradley (12), MacEwan (56) and Green-Kelly (33) working with a great number of alcohols and benzene-ring compounds found that the more polar materials could enter between the structural sheets of the clay minerals. Ensminger and Giesecking (21) and Talibudeen (77) have demonstrated that large protein molecules also can penetrate between the clay mineral layers and create wide 001 lattice spacings. Greenland (34), and Lynch et al. (53) have shown by X-ray studies that carbohydrate materials are also adsorbed in the interlayer positions in montmorillonitic clay minerals. In recent studies on the determination of naturally occurring fixed  $NH_4$  in soil, techniques have been developed in which the silicate clay minerals are destroyed by HCl- HF treatment. Nitrogen determination before and after

this destruction of the mineral has shown that both organic and inorganic N are released from between the clay mineral layers by this treatment.<sup>1</sup> Thus, there is evidence that organic materials do exist between the clay mineral layers.

The presence of such materials between the lattice layers of soil clay minerals could enhance the adsorptive properties of the oven-dried materials because it would prevent the lattice from contracting. The lattice would then be sufficiently expanded even in an oven-dried state to allow non-polar molecules like  $O_2$  to enter and be adsorbed on the internal surfaces. Treatment with  $H_2O_2$  did not affect the  $O_2$  adsorbed by Edina subsoil or illite, but it is expected that organic materials between the plates would not be accessible to action by the peroxide. Therefore, to pursue this possibility further, the opposite approach was used. That is, the effect of placing organic materials between the interlayer positions of the clay minerals was determined.

Edina subsoil and bentonite samples which were oven-dried at  $110^\circ C$ . were saturated with ethylene glycol and then oven-dried for 48 hours in a porcelain dish. A sample of air-dried bentonite was also treated with gelatin using a modification of the procedure described by Gieseking (32). A

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<sup>1</sup>Bremner, J. M. Rothamsted Experimental Station, Harpenden, England. Nitrogen release from soil clays by HCl-HF treatment. Private Communication. 1958.

10:1 ratio mixture of bentonite to gelatin was prepared in an excess of water and heated to  $100^{\circ}$  C. The pH of the mixture was adjusted to 4 and the excess moisture filtered-off on a Buchner funnel under suction. The slurry was washed with hot water, air-dried, passed through a 0.5 mm. sieve and oven-dried for 48 hours. Oxygen adsorption isotherms were determined with the glycol and gelatin treated materials after they were oven-dried for 48 hours at  $110^{\circ}$  and  $250^{\circ}$  C. The results obtained are compared in Figures 32 and 33 with untreated, but similarly dried materials.

When the Edina subsoil was saturated with ethylene glycol and oven-dried at  $110^{\circ}$  C., its adsorptive capacity was decreased (Figure 32). Since glycol has a boiling point of  $197^{\circ}$  C., most of the glycol adsorbed by the soil was still present after the  $110^{\circ}$  C. drying. This glycol apparently prevented the adsorption of  $O_2$ . This effect is probably comparable to that from adsorbed water because on heating to  $250^{\circ}$  C. adsorbed glycol was removed and the adsorption of  $O_2$  increased. The glycol treated sample adsorbed slightly more  $O_2$  than the untreated sample after they were heated at  $250^{\circ}$  C. This could be due to the entrapment of some glycol between the plates with a resulting increase in the internal surface accessible for adsorption by dry soil.

The glycol treated bentonite which was oven-dried at

Figure 32. Effect of ethylene glycol on the amount of  $O_2$  adsorbed by  
Edina subsoil sample 2

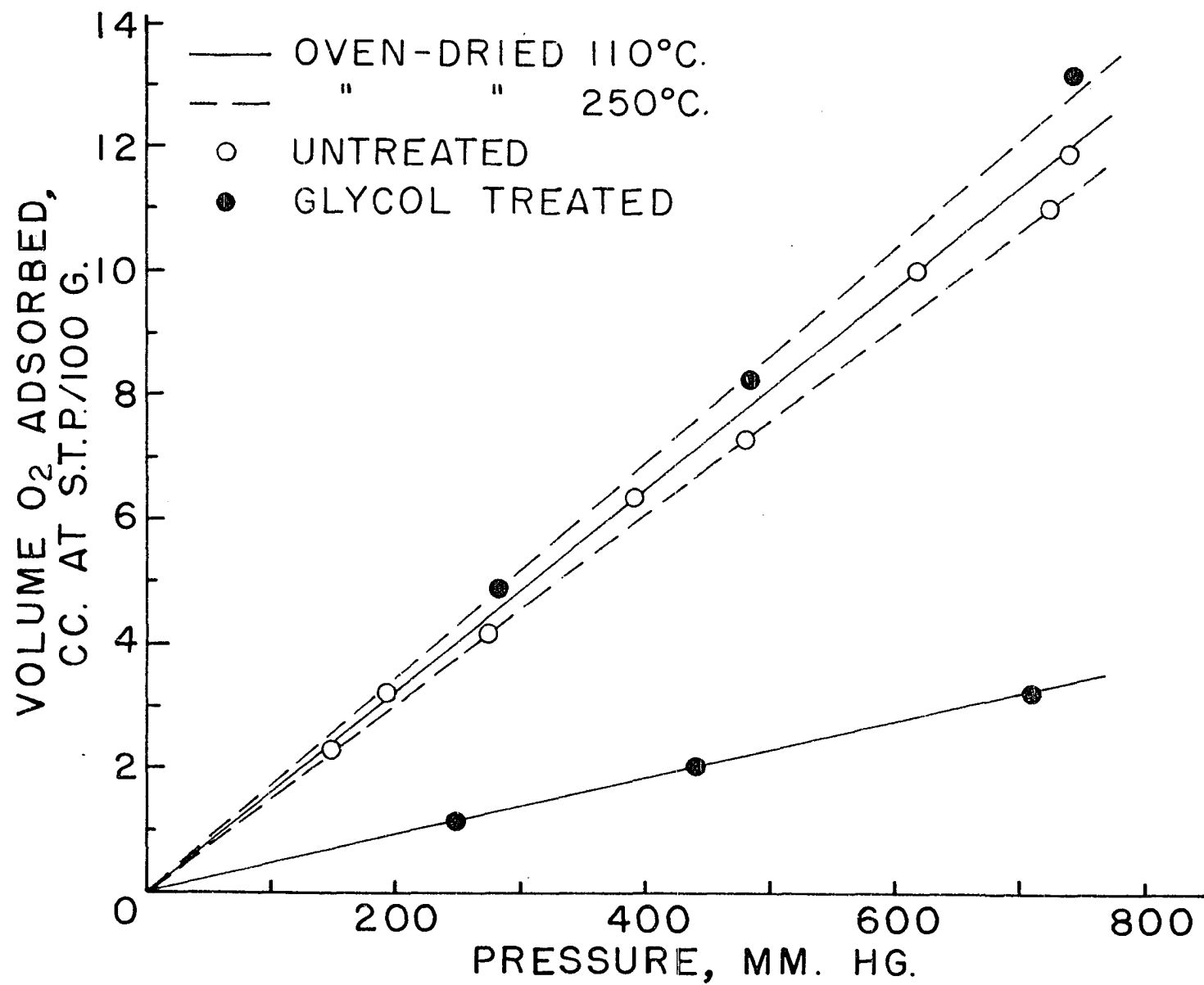
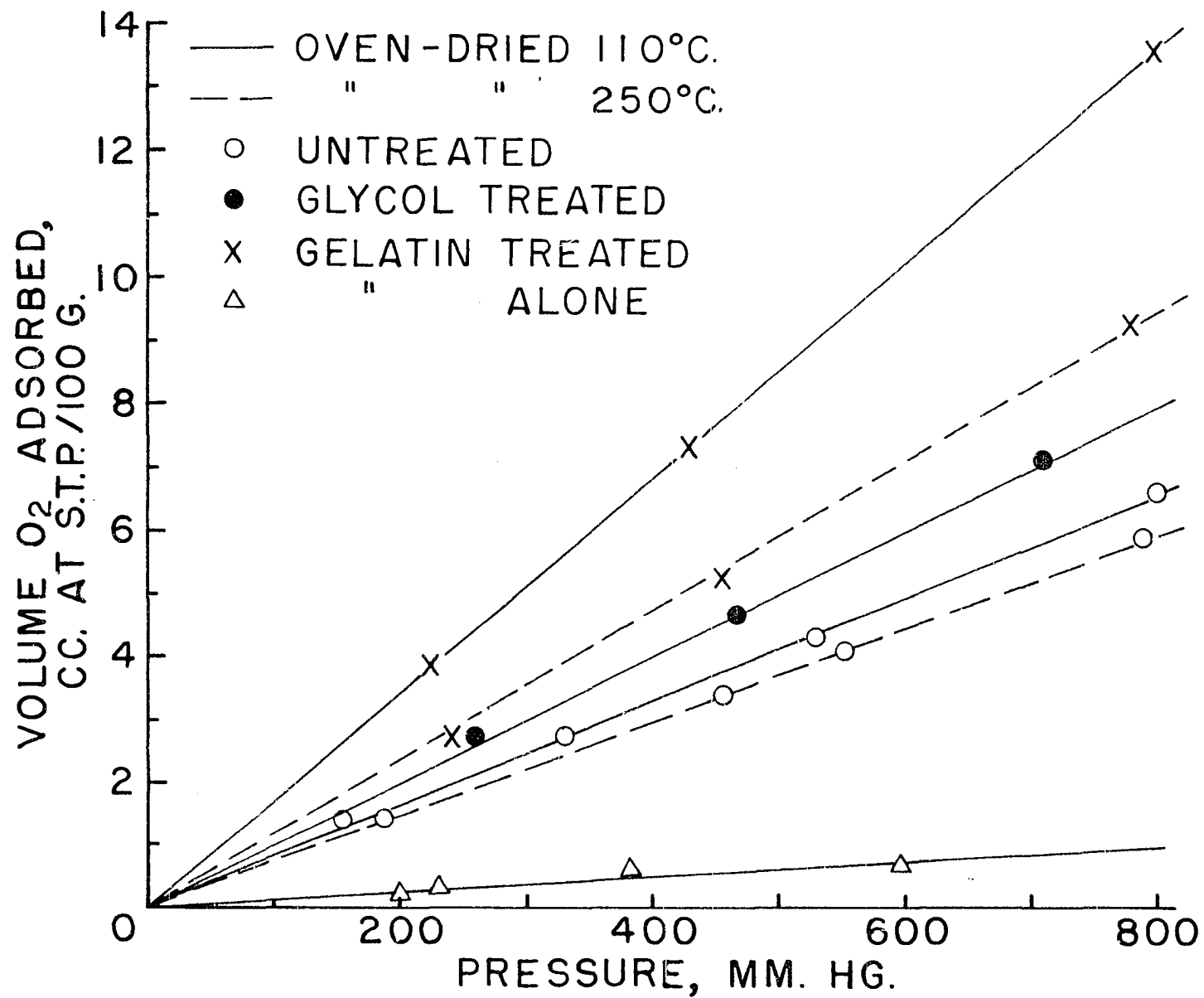


Figure 33. Effect of ethylene glycol and gelatin on the amount of  $O_2$  adsorbed by bentonite



110° C. exhibited a slightly greater adsorption of O<sub>2</sub> than the untreated bentonite (Figure 33). It is well established that glycolated bentonite exhibits an 001 spacing of 17<sup>0</sup>Å. The clay plates were thus far enough apart for O<sub>2</sub> gas to enter the lattice, but again as in the case of the Edina subsoil the adsorbed layer of glycol limited O<sub>2</sub> adsorption just as water does.

The gelatin treated bentonite adsorbed more O<sub>2</sub> than the untreated bentonite. This increase in adsorption cannot be accounted for by adsorption by the gelatin itself. In the first place, the adsorption of O<sub>2</sub> by gelatin per 100 g. was measured and found to be very low. Also, the amount of gelatin present in the bentonite was low because the clay mineral was washed with hot water to remove as much of the excess gelatin as possible.

Giesecking (32) has reported an interlamellar spacing of 27<sup>0</sup>Å for 105° C. oven-dried, gelatin treated bentonite compared to a 12.0<sup>0</sup> Å spacing for the air-dried, untreated sample. The interlayer spacing would thus be wide enough for O<sub>2</sub> to penetrate between the lattice plates and the observed increase in adsorption would indicate increased adsorption by internal surfaces did occur. Nelson and Hendricks (65) attempted to increase surface adsorption by treating montmorillonite with brucine, which gives a 16.5<sup>0</sup> Å separation,



but they were not successful.

The volume of  $O_2$  adsorbed by the gelatin treated bentonite was comparable to that adsorbed by the untreated Edina subsoil, 13 cc./100g. versus 12 cc./100g. The adsorption volume for bentonite is still small, however, when the clay content of bentonite is considered in relation to that of the Edina subsoil. Bentonite has 90%  $<2\mu$  size fraction, while Edina has 52%. Thus, the internal surface of the gelatin treated bentonite accessible for  $O_2$  adsorption was still less than that in Edina.

A decrease in adsorption occurred when the gelatin treated bentonite was heated from  $110^\circ$  to  $250^\circ$  C. This decrease in adsorption due to heating is similar to that observed when the soils were heated from  $110^\circ$  to  $250^\circ$  C. The gelatin and probably the organic materials between the layers of the soil clay minerals are not volatile. The reason for the decrease in adsorption due to heating to  $250^\circ$  C. and to  $500^\circ$  C. in the case of soils is, thus, not apparent. Since untreated bentonite and kaolinite which contained no organic matter did not show this decrease, whereas soils and bentonite treated with a non-volatile organic substance did, the decrease must be associated in some way to the existence of these organic molecules in the system. The gelatin treated bentonite dried at  $250^\circ$  C. still adsorbed more  $O_2$  than the similarly heated, untreated bentonite.

## SUMMARY AND CONCLUSIONS

The sorption of  $O_2$  and  $CO_2$  at  $25^\circ C$ . by moist illite, vermiculite, kaolinite and bentonite clay mineral samples and by moist Edina and Fayette subsoil samples was investigated. The moist materials were progressively dried and the amount of gas sorbed by the materials at different moisture levels was determined with a volumetric technique. The experimentally determined sorption values were compared in each case with the theoretical solubility of the gas predicted by Henry's law.

The amount of gas sorbed by the moist samples was found to be a function of the moisture content. In general, at moisture contents above 10 to 15%, the sorption of  $O_2$  could be related to the solubility of the gas in the soil water assuming that this water behaved like pure water. The clay mineral and exchangeable cations apparently did not cause any salting-out effect at these moisture levels. Moist natural bentonite and one of the Edina subsoil samples were exceptions in that their  $O_2$  solubility values were less than the theoretical solubility of  $O_2$  in pure water. These sorption values were probably low because part of the water was not accessible for the solution of  $O_2$ . This could occur if the water was in an interlayer position or if salting-out effects from the exchangeable cations and clay surfaces existed.

When the Edina subsoil sample was moistened to a higher moisture level prior to the sorption study, this discrepancy disappeared. Bentonite, on the other hand, gave low sorption values even though the sample was moistened to 80% moisture. It does not appear likely, however, that salting-out effects would be apparent at this high moisture level. Therefore, since these Edina and bentonite samples were initially air-dry, it appears more likely that the low sorption values occurred because interlayer water was not accessible to the  $O_2$ . That is, the values were low because of the experimental procedure used.

In general, the results obtained with moist soils and clay minerals would indicate that salting-out effects are negligible in the moisture range encountered in field moist soils. Thus, the amount of sorbed  $O_2$  in a field moist soil is essentially the same as the amount of dissolved  $O_2$  predicted by Henry's law.

The amount of  $CO_2$  sorbed by moist vermiculite at the high moisture levels was comparable to the solubility of this gas in the water present. Edina subsoil, illite and kaolinite, however, sorbed more  $CO_2$  than that which could be accounted for by the solution of  $CO_2$  in pure water. When the water was gradually removed from these moist samples, the volume of  $CO_2$  sorbed decreased in the same proportion as

the theoretical  $\text{CO}_2$  solubility. The reason for the high  $\text{CO}_2$  sorption values was not investigated.

The gas sorption values exceeded the gas solubility values predicted by Henry's law when the moisture content was less than 10 to 15% in the soils, kaolinite and vermiculite, and less than 20% in the bentonite. Furthermore, there was a rapid increase in the sorption values when the moisture content was decreased below these levels. To determine if these sorption values were also related to the solubility of the gas an expression for the solubility of a gas in water was derived to take into account deviations from Henry's law due to salting-out and capillary effects. Oxygen solubility values were calculated with this expression and compared with the experimentally determined sorption values for the moist Edina and Fayette subsoil samples. The amount of soil water that was unavailable for the solution of  $\text{O}_2$  because of salting-out effects or because of inaccessibility in inter-layer positions was not known. Therefore, it was assumed in these calculations that no water was unavailable. Also, for these calculations the water vapor pressure values for the soils were needed. The water vapor pressure of the moist samples was, therefore, determined with the same volumetric apparatus prior to each sorption measurement.

The  $\text{O}_2$  solubility values calculated on this basis were

comparable to the experimentally determined sorption values for samples containing more than 5% moisture. The initial decrease in water vapor pressure and the initial increase in gas sorption observed when the moisture content was decreased below the 10 to 20% level was therefore primarily due to capillary effects. No salting-out effects were evident in these soil samples. If they occur at even lower moisture levels they would necessarily be small because the total amount of water in the samples that could dissolve  $O_2$  was very small. Also, in the very low moisture range there was a rapid increase in sorption due to the process of adsorption when water was removed. Thus, salting-out effects in this moisture range would not be observed if they did occur.

There was a continuous increase in the amount of gas sorbed by the soils, kaolinite, vermiculite and illite when the samples were dried, from about 5% moisture to a  $110^\circ$  C. oven-dry state. Apparently the clay surfaces were able to adsorb more gas when the water was removed. Bentonite, on the other hand, exhibited first an increase and then a decrease in the amount of gas sorbed in the same moisture range. Apparently some increase in adsorption occurred when the water was removed, but the lattice must have contracted when more water was removed and as a result there was less surface available for gas adsorption.

A comparison of the  $O_2$  and  $CO_2$  adsorption values for  $110^\circ$  C. oven-dried soils and clay minerals showed that some soils adsorbed more gas than bentonite. The samples were, therefore, oven-dried at  $110^\circ$ ,  $250^\circ$ ,  $500^\circ$  and  $750^\circ$  C. to determine the effect of the drying temperature on adsorption. The adsorptive capacity of  $110^\circ$  C. oven-dried materials was also related to the clay and organic matter content of the materials.

Linear  $O_2$  adsorption isotherms and curvilinear  $CO_2$  adsorption isotherms were obtained for all of the materials that were heated at  $110^\circ$ ,  $250^\circ$ ,  $500^\circ$  and  $750^\circ$  C.

There was a decrease in the adsorptive capacity of the soils and illite when the heating temperature was increased. Little change occurred in the other clay minerals until the temperature was increased to  $750^\circ$  C. The adsorptive capacity of some soils continued to be greater than that of bentonite even after they were heated at  $500^\circ$  C., but the higher temperature apparently had some effect on the soil property that caused this difference.

A linear relationship between the clay content and the adsorptive capacity of the  $110^\circ$  C. oven-dry soils was observed. The clay minerals from natural deposits did not fit this relationship. Thus, it is evident that soil clay miner-

als may behave differently from natural deposit clay minerals of the same type.

The adsorptive capacity of these materials was not related to their organic matter content. Also, the removal of organic matter with  $H_2O_2$  had little effect on their ability to adsorb gases. Nevertheless, it is suggested that the occurrence of organic materials between the lattice layers of the soil clays accounts for the difference between them and bentonite. This suggestion is supported by the observation that illite, which contains organic matter behaved more like the soils. Also, when bentonite was treated with gelatin, which can be adsorbed between the lattice layers, more gas was adsorbed. Apparently organic materials between the lattice layers prevent the clay mineral lattice from contracting when the material is dried. Thus, in a  $110^\circ$  C. oven-dried state the internal surface of the mineral is still accessible for the adsorption of non-polar molecules.

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